Chemical recovery from chromated copper arsenate wood preservative sludges

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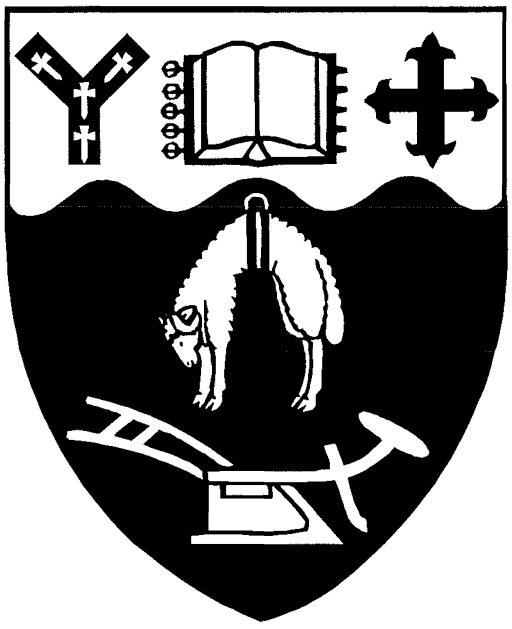

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To Simone, my inspiration,

and my father Robert, who listened

Abstract

Chemical recovery from chromated copper arsenate wood preservative sludges

A number of aspects of the chemistry of chromated copper arsenate wood preservative (CCA) are investigated. The environmental hazard posed by CCA is briefly reviewed, and the need for a method of handling chemical wastes, such as treatment plant sludge, is stressed. The nature of a particularly chemical sludge is elucidated via a wide range of spectroscopic techniques including powder XRD, ICP-OES, automated light element analysis, XRF, TGA/DTA, UVA, FTIR, and XAFS, and it is concluded that the principal mechanism of formation is extensive oligomerisation of chromium (III) arsenate complexes at or below a critical pH of 2.3. Though this sludge can be dissolved relatively conveniently in arsenic acid and thereby returned to the manufacturing process, this is found to be unsatisfactory except in very small quantities since the spent chromium (III) component will accumulate during subsequent treatments. A method for extracting the arsenic (V) cheaply and easily under strongly basic conditions is presented. It is shown that the chromium (III) cannot be reclaimed effectively by chemical oxidation, but a novel method for electrochemical oxidation in a chemically and economically viable fashion is developed. The literature concerning the chemistry of CCA fixation in wood is critically reviewed, and new models for the reaction of preservative with wood and the nature of the fixation products are proposed; the principal reducing groups are to be guaiacyl rings in lignin and primary alcohol functionalities in both lignin and carbohydrates, while the final fixation products are to consist of wood carboxylate- copper (II) complexes, chromium (III) arsenate and chromium (III) hydroxide. Treated wood has been analysed by the powerful modern XAFS technique and results consistent with this model have been obtained.

Contents

Conventions

References [ref] are listed at the end of each chapter according to the order in which they appear in the text. *Digressions* from the main argument are italicised, and sections generally finish with a boldface **conclusion**.

Unless otherwise stated, all chemicals used in this study were analytical reagent grade, and all chemical data were taken from the Handbook of Chemistry and Physics (77^{th} ed.) or Merck Index (11^{th} ed.).

The expression (N) following the name of an element indicates its formal valence state; the superscript $^{n+}$ is only used for the 'free' aqueous ion. The sign $\approx$ means 'approximately equal to'. All electrochemical potentials are stated as reductions with reference to the standard hydrogen electrode. Where the reaction is an oxidation, the reduction potential for the reverse reaction is given in parentheses. In tables and figures, the units of measurement are generally given in parentheses.

CCA is frequently used as an abbreviation for 'chromated copper arsenate wood preservative', and FTP is the acronym for Fernz Timber Protection Ltd. (N.Z.), the industry partner: Fernz Timber Protection Ltd. (N.Z.), 14 Mayo Rd., Wiri, P.O.Box 88-048, Clendon Town, Auckland, New Zealand; tel. +64-9-277-7770, fax +64-9-277-8011.

Introduction

> *"he made me the gift of that pile of old sins: I should think about it, make tests and examinations, and try to say with precision why the trouble had occurred, what should be done so that it was not repeated, and if it were possible to reclaim the damaged goods. Thus set forth, half chemistry and half police work, the problem attracted me..."*
>
> Primo Levi, *The Periodic Table*, "Chromium", pp. 153

The degree of Doctor of Philosophy in Environmental Science is new to the University of Canterbury. Indeed, there has only been one previous graduand, Stanley van den Assem, who examined dispersion of air pollution in the Christchurch area. Environmental science is taught as an interdisciplinary subject, jointly administered by the Departments of Geography, Geology, Plant and Microbial Sciences, and Zoology. As a physical scientist, my entry into this natural preserve was somewhat unusual, yet it was greatly facilitated and indeed encouraged by the first Environmental Sciences Coordinator, Dr. Vida Stout, and the Head of the Department of Chemistry, Dr. Colin Freeman.

I feel that the connection is more than appropriate, indeed mandatory, and I hope that it continues to grow in future years. In my opinion, the spirit of chemistry lies in the ability to transform one thing into another. The word itself comes from an ancient phrase for 'the Egyptian art', transmutation. The derivation is less obscure in other languages; for example, in Japanese it is *ka-gaku*, 'the study of change'. Chemistry should then be profoundly active in nature. Therefore it must be fundamental to environmentalism, which is based on the principle of 'thinking globally, acting locally'. That chemistry does not concern itself with the 'vital' characteristics of systems is irrelevant.

This project began with the general intention of **avoiding, remedying, or mitigating some of the environmental concerns associated with the use of chromated copper arsenate timber preservative (CCA)**. To my mind, the motivation is sufficient to classify it as environmental science rather than pure chemistry. Further, the chemical reader may well consider the generalist approach somewhat utilitarian. Certainly, once a path was shown to be impractical, the search for a chemically complete answer was abandoned. One exception was the X-ray absorption fine structure spectroscopy discussed in Chapter Seven. Nonetheless, I believe that the project constitutes a thorough investigation of the issue, and trust that the conclusions are useful and original enough to warrant it.

Dr. Peter Harland of the Chemistry Department volunteered to supervise the project, despite many other pressing commitments. Peter's commonsense, efficiency, and diligence were indispensable, and I am most grateful to him. Secondary supervisors were Dr. Jack Fergusson, Dr. John Walker of the School of Forestry, and Mr. Iain Gilmour of Chemical and Process Engineering. Almost every academic or technical member of Chemistry Department staff was consulted during the project, but particular thanks go to Prof. Don House, Mr. Russell Gillard, Mr. Danny Leonard, Mr. Wayne Mackay, and Prof. Ward Robinson. Thanks are also due to the Academic Board, and E.W. Roper, for the Roper Scholarship in Science which supported me during the first year.

An early approach to Dr. Sandy McQuire, an eminent authority on the use of CCA in New Zealand, produced depressing results. Dr. McQuire clearly felt that the project was a waste of time; in his words, "the industry doesn't think there's a problem". As he must have known, this statement was somewhat in error. J.M. Duignan had presented a paper to the New Zealand Wood Preservers' Association annual general meeting in 1982, raising a number of environmental concerns. Eight years later, at a wood preservation industry symposium in Rotorua, Dr. Mike Freeman said "It is self-evident... that the existing codes of practice, regulations and/or the way in which they are implemented are not providing an adequate level of environmental protection... some plant operators/owners are generally unaware and/or not interested in fully meeting their environmental obligations". Some details of the problems in New Zealand will be given in Chapter One.

A talk I gave at the University of Canterbury's Wood Technology Research Group conference of October 1996 stirred up an industry partner who was both interested and supportive. Frank Frazer was the technical development manager of Chemicca Ltd., an Auckland company which produced around half of New Zealand's CCA. Apart from a general interest in the chemistry of CCA, Chemicca had somewhat unwisely accepted tens of thousands of litres of CCA chemical wastes from customers. This material took up a substantial amount of their warehouse space, not to mention the balance sheet.

With the backing of general manager Mike Brown, Frank helped us obtain a Graduate Research in Industry Fellowship (GRIF) from the New Zealand Government's Foundation for Research Science and Technology. This fellowship provided a small amount of money for the University, and a generous amount for myself which more than offset the cost of spending half my time in Auckland. Chemicca were kind enough to pay my airfares, part of my accommodation costs, and many project expenses as well.

Shortly after my arrival, Chemicca was taken over by Fernz Corporation, and became Fernz Timber Protection Ltd., N.Z. (FTP). The GRIF arrangement was honoured by John Lea, the new general manager, but Frank was replaced by Dr. Tony Bergervoet. Tony's experience and enthusiasm deserve much of the credit for the successes of the project.

1 CCA and the environment

Chromated copper arsenate timber preservative, CCA, has been used extensively worldwide for more than forty years. It greatly increases the service life of timber which is exposed to weather, in ground contact, or immersed in water. CCA exhibits broad spectrum toxicity based on the fungicidal properties of copper and the insecticidal properties of arsenic. The principal function of the chromium is to drive the reactions which 'fix' the preservative strongly into wood. Typical retentions of active elements are several kilograms per cubic metre of wood; in the United States of America alone, the yearly output is approaching twenty million cubic metres[1]. Other users include Canada, India, Australia, the Scandinavian countries, Germany, Japan, South Africa, and New Zealand (0.5 Mm^3y^{-1}). In normal conditions, the active components remain in properly treated timber throughout its service lifetime[2]. Nonetheless, CCA is a potent poison which is effective because it is bioavailable and persistent. Inevitably its use has caused environmental problems.

Timber treatment plants are generally small-scale operations. In the process, a dilute aqueous solution of CCA is forced deep into the timber by an applied pressure of 1400 kPa. Reduction of chromium (VI) to chromium (III) by wood components leads to the formation of insoluble precipitates and wood-ion complexes[3,4,5,6]. The active elements are chromium (VI), copper (II), and arsenic (V) in varying proportions, though modern CCAs have molar ratios around 6:3:4. The less corrosive 'oxide' formulations are made from chromic acid, arsenic acid or arsenic pentoxide, copper oxide or hydroxide, and possibly copper arsenates. 'Salt' or 'sulfate' formulations may include copper sulfate and sodium or potassium dichromates, arsenates, or pyroarsenates.

Free chromates and arsenates can pose a significant hazard to the environment. Reduction to arsenic (III) increases toxicity substantially, while chromium (III) is relatively harmless.

Table 1.1 Soil acceptance criteria for CCA elements [7]

Use	Contaminant, ppm			
	Arsenic	Chromium (VI)	Chromium (III)	Copper
Background	*2-30*	*NA*	*<4-220*	*0.1-110*
Agricultural	30	4	600	40
Residential	30	9	600	80
Industrial paved	650	510	NL	1000
unpaved	500	360	NL	570

Table 1.2 Water quality guidelines for CCA elements [7]

Use	Contaminant, mgL^{-1}			
	Arsenic	Chromium (VI)	Chromium (III)	Copper
Potable	0.01	0.05		1
Stock	0.5	1		0.5
Irrigation	0.1	0.1		0.2
Recreation	0.22	2.2	42	22
Ecosystem	0.19	0.011	0.12	0.0065

Chromium (VI) and inorganic arsenic are also mild carcinogens, rated 1A by the International Agency for Research on Cancer.

Generally, environmental legislation and industry codes of practice exist to minimise the risk of pollution. For example, active preservative can readily enter the environment through spillage, or through drip from recently treated timber. So, in New Zealand, the Department of Labour's Code of Practice[8] requires all treatment plants to have retaining areas, or "bunds", sufficient to contain any spills from holding tanks. Drip is to be avoided through application of a final vacuum while the timber is still in the treatment cylinder, and timber must be kept on a sealed drip pad for at least 48 hours. Washings from the drip pad must be collected and recycled. There are also provisions to prevent rainwater or stormwater mobilising CCA.

Nonetheless, there have been a number of acute incidents in the last twenty years[9,10,11], and the situation regarding chronic pollution of point sources may be much worse. Some Bay of Plenty sites are known to be contaminated to several thousand ppm with CCA elements[12]. Arsenic, copper (II), and chromium (III)- but not necessarily (VI)- are readily immobilised by most soils[13,14,15,16], so these problems are not widespread. Still, there are some contaminated sites in New Zealand whose pumice soils do not have this property, since pumice is very low on iron- and aluminium- based absorber sites. In these places, CCA must have gone straight down into the groundwater[16,17]. In other countries, there have recently been some attempts to clean up such sites. Approaches have included electrodialysis[18] and soil washing[19], though the "least worst" course of action may often involve leaving them alone[20].

Chemical wastes from CCA treatment present a similar hazard. In particular, "sludging" reactions in CCA work solution lead to the precipitation of treatment plant sludge during and after treatment. In adverse conditions, more than 5% of preservative can be wasted in forming sludge. This pale green solid is well known to be rich in the three CCA elements, and to fail standard toxicity characteristic leaching profile (TCLP) tests for all of them[21]. That makes it a toxic waste, needing careful and expensive disposal. In New Zealand dumping in designated secure landfills is deemed sufficient, but other countries, such as Australia, require immobilization in concrete[22,23].

The safety or otherwise of CCA-treated wood has been the subject of some extravagant claims[24,25]. Providing that the fixation reactions are complete, and that there are no deposits of excess preservative on the surface[26], there is a reasonable consensus that it is nonhazardous under normal service conditions[2,27]. However, leaching may have detrimental effects upon estuarine environments[28]. Chelating organic acids such as citrate can promote leaching[29,30] which raises concern over exposure of treated wood to humic substances. Certainly, treated wood should not be used for storing silage or compost, or drastic leaching will result[31,32]. In New Zealand kiwifruit orchards, bacterial attack has been observed to destroy properly treated posts in as little as three years[33,34,35]. There may be a connection, which has not been drawn elsewhere, with the practice of spraying with citric acid to control the kiwifruit ripening process.

In any case, all treated wood must eventually break down, releasing the preservative elements. A vast amount of treated timber is projected to leave service in the coming decades, and it would be highly preferable to find some alternative to landfilling this potentially hazardous material[36,37,38,39]. Treated offcuts, sawdust, and such present a similar problem[40] which seems to be frequently overlooked. Although it is strictly forbidden, it is probable that much of this waste is burned at the point of origin. Treated wood cannot readily be burned safely, since most of the arsenic fraction is readily volatilised as arsenic (III)[41,42,43]. The ash is also highly toxic since it retains the rest of the heavy metals. This practice, which certainly occurs in New Zealand, can lead to widespread contamination[44].

One ingenious exception was identified by Nurmi and Lindroos[45], who fed used treated wood chips into a flash smelting furnace at a major copper smelter. Since copper ores often contain arsenic and other metals, this caused no interference in the smelter's operations, indeed the heat from burning the wood made for a small energy saving. Copper and arsenic were recovered. Unfortunately, few operations have ready access to a copper smelter, and they are themselves notorious polluters.

Incorporation of used CCA-treated wood into composites risks creating a larger disposal problem. Manufacturers of particle board appear resistant to the idea[39], and anyway, the usual adhesives used in particle boards do not bond the "salty" treated wood well. Conversely, treated wood appears superior to untreated wood for use in wood-cement composites[46].

Surprisingly, composting has met with considerable success in the medium term, since many plants seem able to accumulate CCA elements in their roots yet exclude them from the above-ground portion[47,48,49].

Still, the problem would be much less serious if the CCA elements could be extracted from the wood. Since the resistance of the preservative to leaching is considerable, this is a very difficult task. Honda *et al.*[50] successfully extracted with excess 0.25 M sulfuric acid at 80 °C over several hours, but this harsh process is expensive. Further, the acidic and highly degraded wood waste would be difficult to use elsewhere. Subsequently, Stephan and co-workers had some success with organic acids[51] and bacteria[52].

Fortunately, some excellent results have recently been published. Kazi and Cooper[53] were able to extract 95% of the chromium, 100% copper, and 88% arsenic at 50 °C with two hours in 10% formic acid, followed by two hours in 10% oxalic acid. Clausen and Smith[1] employed 1% oxalic acid, then steam explosion, and finally fermentation with the bacterium *Bacillus licheniformis* CC01 to remove 80% of the chromium, 90% copper, and 100% arsenic. So far, the fate of the inorganic extraction products has not been considered in the literature. Processes like these which do not involve reduction or oxidation reactions must generate wastes rich in chromium (III), copper (II), and arsenic (V), resembling the chemical sludges from CCA treatment plants. If the CCA elements can be removed from contaminated sites, it will most likely lead to similar materials. But there is no environmentally or economically sound method for dealing with such wastes at the moment.

Thus it is the chemical wastes which are the key; the next step in reducing the environmental hazard presented by this otherwise useful preservative lies in developing a method for recycling sludge.

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2 Characterisation of treatment plant sludge

Current methods to mitigate or remedy sludging are essentially empirical. This is unavoidable because there is no consensus as to what exactly sludge is, or how it is formed. Dahlgren and Hartford's seminal work on fixation[1,2,3,4] considers the likely states of chromium (III) and copper (II) in the presence of arsenate and chromium (VI) anions. In a regime of decreasing acidity, driven by the reaction

$$CrO_4^{2-} + 8H^+ + 3e^- \longrightarrow Cr^{III} + 4H_2O$$

a number of precipitates should form, the final stable states being $CrAsO_4$ and $Cu_2(OH)AsO_4$. The bulk solution should never reach pH 3.2, at which point $Cu_2(OH)AsO_4$ precipitates[4]. Therefore sludge should be dominated by chromic arsenate, which precipitates at a relatively low pH. A number of elemental ratios have been published which are consistent with this view[5,6,7].

Table 2.1 Reports of simple analyses for CCA elements in sludge

Author	% Cr	% Cu	% As
Mutandadzi & Evans	19.7	3.2	41.4
Butler	13 - 19	2 - 7	23-30
Judd	14.5	3.1	23.5

The Mutandadzi and Evans figures have similar elemental ratios to the other two, but different absolute concentrations. Converting arsenic weight to arsenate, their figures total 100%, so it seems likely that they have been scaled. Similar ratios were also obtained by Thom and Nash[8], who analysed sludge slurries without calculating back to concentrations in the solid fraction.

The only papers to make detailed analysis of sludges obtained dramatically different results. Pizzi *et al.*[9] attempted to obtain multivariate regression equations for the extent of CCA fixation under varying conditions. In the process they produced sludges, which were analysed for Cr, Cu, and As content by atomic absorption spectroscopy. From the percentage contents alone, the sludges were identified as mixtures of chromium arsenate, copper chromate, and a copper arsenate denoted $CuAsO_4$ (not a credible formula).

Unfortunately, given the nature of AAS, any such ionic or molecular identification can only be based on conjecture. This technique will readily give the amounts of chromium, copper, and arsenic present in a solution. It cannot distinguish between chromium (III) and chromium (VI). It cannot establish that cupric ion is bound to the chromate while chromic ion is bound to the arsenate. And since copper chromate is intensely yellow and quite soluble, it is unlikely to be found in pale green precipitates.

Copper arsenate was said to be dominant in sludges from working solutions with initial pH > 2.8. That is reasonable, since $Cu_2(OH)AsO_4$ will precipitate under those conditions. It follows that the solutions cannot have been stable, which probably invalidates those particular experiments. Those conditions should not occur in treatment plants.

Further, Pizzi et al. have serious flaws in their statistical analysis. All of the equations are based on less than thirty data points, many on only nine. This is too few to justify a multivariate nonlinear treatment, particularly when sophisticated variables like $^{(temperature)\times(concentration)}/_{\sqrt{pH}}$ *are used. Some of the expressions even use pH as a variable when it is being held constant!*

In a previous paper, Pizzi *et al.*[10] obtained different sludges from the bulk treatment solution and from that part of the solution expelled from the wood during the final vacuum phase of the treatment. Both sludges were said to contain copper chromates, chrome arsenates, and copper-carbohydrate complexes; the solution from inside the wood was also said to contain copper arsenates. Again, the analysis was by AAS, so the same objections apply. Further, there was no analysis for carbon, let alone carbohydrate.

Worse, their freshly prepared solution sludged to an unacceptable degree just on standing, without any contact with wood, meaning that it was quite atypical. Any commercial user would indignantly reject such a product. The precipitate thus formed appears to have made up the great majority of the sludge collected in their treatment experiments. Since it was not formed from reaction with wood, their overall result is scarcely rigorous.

It is surprising that these two papers have been accepted so readily into the literature. A new detailed analysis seemed imperative.

The selected representative sludge was produced by a single treatment company who invariably processed *Pinus radiata* using the alternating pressure method (APM). In APM, the CCA solution is driven into the wood by several 1400 kPa pressure cycles. Air trapped in the wood cells is compressed. It expands in a "kick-back" at each release of pressure, pushing solution out of the wood, so that some reacting preservative precipitates outside the wood instead of inside. Wood extractives are also released into bulk solution to react separately. The overall result is a "quick and dirty" treatment which enables rapid turnover but can result in extensive sludging. Since this sludge builds up quickly, the proportion of foreign material is low.

FTP had about 10,000 L of this material on hand, in a single tank. Despite several months' storage the sludge had not completely settled, varying from a thin, yellow-tinged suspension to a green clay. The supernatant was decanted, and the 'clay' oven-dried at 60 °C to yield a dull, clumpy, pale green powder, which was used for all the following analyses.

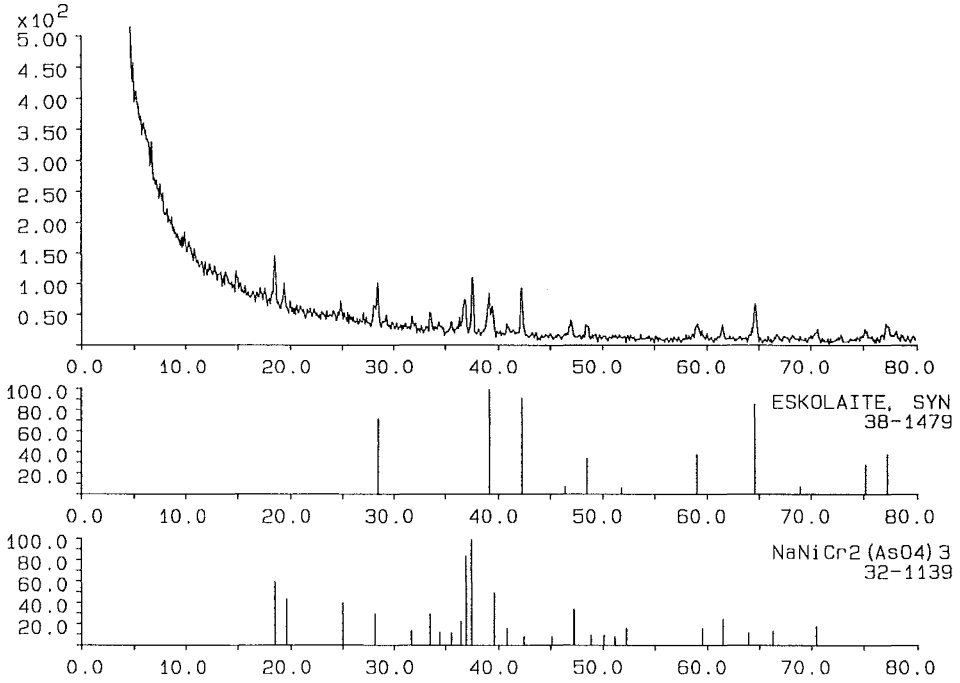
The initial powder X-ray diffraction (XRD) spectrum was very kindly collected by Prof. J.H. Johnston, Chemistry Department, Victoria University of Wellington, using a Phillips diffractometer, copper K_α radiation, graphite monochromator, scan rate $^1/_4°(2\theta).min^{-1}$, time constant 10. Duplicate samples for inductively coupled plasma optical emission spectroscopy (ICP-OES) were completely digested in aqua regia and run on an appropriately calibrated Thermo Jarrell Ash- Atomscan25 by Campbell Microanalytical Laboratories, Dunedin, N.Z.. The same laboratory used a Carlo-Erba CHNS/O 1108 elemental analyser for the automated light element analysis. Spectrachem Analytical, Wellington, N.Z., used a Siemens SRS 303-AS to obtain semiquantitative X-ray fluorescence (XRF) data, optimising on oxygen. Coupled thermogravimetric / differential thermal analysis (TGA/DTA), ramping at 10 °C.min^{-1}, and powder XRD of the residual solids were undertaken by Industrial Research Ltd., Gracefield Research Centre, Wellington, N.Z.. The author conducted ultraviolet absorption spectroscopy (UVA) using a Hewlett-Packard HP8452A diode array ultraviolet-visible spectrophotometer, and Fourier transform infrared spectroscopy using a Shimadzu FTIR-8201PC and GmbH Spectacle® software with Happ apodisation and a resolution of 2 cm^{-1}.

$CrAsO_4$ was prepared by complete reduction of H_2CrO_4 by excess H_2O_2 in the presence of excess $Na_2HAsO_4{\cdot}7H_2O$. The precipitate was removed by vacuum filtering, washed thoroughly with distilled water, and oven-dried at 60 °C. Similarly, $Cr_2(SO_4)_3$ solution was prepared by complete reduction of dilute H_2CrO_4 by H_2O_2 in the presence of a slight excess of H_2SO_4. The solution was boiled for four hours to destroy unreacted peroxide, cooled, and made up to known volume.

Powder XRD yielded an almost featureless spectrum, implying that the powder was either amorphous or inhomogeneous. This is not enough information to "fingerprint" against reference patterns.

Sludge does become crystalline when fired to 900 °C under oxygen-free nitrogen (OFN). The powder XRD spectrum is shown in Figure 1. The accompanying mineral spectra appear to account for all the observed signals; "eskolaite" is simply Cr_2O_3.

Figure 2.1 Powder XRD spectrum of fired sludge



ICP-OES showed that chromium and arsenic dominate the sludge, in almost equimolar amounts.

Table 2.2 Major constituents of sludge by ICP-OES

%w/w	As	Cr	Cu	Fe
1	25.4	16.1	3.17	0.19
2	25.6	15.9	3.21	0.23
average	**25.5**	**16.0**	**3.2**	**0.20**

Automated light element analysis gave the following results:

Table 2.3 Carbon and hydrogen content of sludge

%w/w	C	H
1	2.36	2.97
2	2.37	2.95
average	**2.37**	**2.96**

One potential carbon compound is carbonate, known to be formed during CCA treatment via decarboxylation of wood constituents[11], but from such acidic solution it will inevitably be evolved as CO_2. Unless there is a considerable amount of fine wood dust, complexed or adsorbed organic species are the most likely carbon source.

In an effort to determine the cause of kiln brown stain, a common blemish in *Pinus radiata* timber, M^{c}Donald *et al.*[12] used water to displace sap from log sections, then extracted them with hot water. An abbreviated part of their analyses is given below:

Table 2.4 Water-extractable compounds in *P. radiata* [12]

%w/w		Sap	Water
Sugars	sucrose	not detected	15.47
	fructose and glucose		7.15
	others		3.44
Cyclitols	pinitol and pinpollitol	15.90	27.74
	myo-inositol	0.51	1.74
Organic acids	glutamic acid	10.3	1.5
	quinic and shikimic acids	0.3	4.2
Lignin		not detected	5.0

The same compounds will be available to the CCA solution, so they or their derivatives could appear in sludge. When strong sulfuric acid is added to sludge, a caramel odour is given off, and a tarry black precipitate is found on filtering. That is certainly consistent with the presence of sugars.

Semiquantitative XRF, optimising on oxygen, was used to determine the minor constituents [Table 2.5] Because the arsenic concentration was outside the calibrated range, an arsenic value somewhat below the true content was obtained, so that all other elements returned slightly elevated results. For example, the iron value is 0.251% whereas the ICP gave 0.20%.

Table 2.5 Minor constituents of sludge (%w/w)

Na	0.971	Al	0.070	Si	0.181	P	0.039	S	0.585
Cl	0.014	K	0.100	Ca	0.066	Ti	0.005	V	0.013
Fe	*0.251*	Zn	0.005	Y	0.001	Sb	0.258	Pb	0.016

To ensure the arsenic content was within calibration limits, the sample had to be diluted 25-fold with cellulose. To the nearest 0.025:

Table 2.6 Major constituents of sludge by XRF

	As	Cr	Cu	Fe
%w/w	**25.10**	**17.30**	**3.325**	**0.20**

The ICP averages should be considered more accurate, because this analysis was only semiquantitative. Nonetheless the agreement is good.

Summing all the results obtained so far gives a total of 53.6%, without analysing for boron, nitrogen, or oxygen. Nitrogen is unlikely to be present above trace levels. Borates are common wood preservatives, but this company has never used them; boron should also be absent. Therefore the remaining 46.4% should be oxygen. Since the slightest trace of chromium (VI) was observed in the supernatant, all other elements should be in high oxidation states:

Table 2.7 Elemental makeup of sludge (mol.kg^{-1})

As^{V}	3.40	Cu^{II}	0.50	Cr^{III}	3.08	Fe^{III}	0.03
		C	1.97	H	29.4		
Na^{+}	0.42	Al^{3+}	0.02	Si^{IV}	0.06	P^{V}	0.01
S^{VI}	0.18	K^{+}	0.02	Ca^{2+}	0.01	Sb^{V}	0.02

Assuming a general $CH_{1.5}O$ formula for the organic fraction, the oxygen requirement is about 28 mol.kg^{-1}, 45% w/w; the mass balance is quite satisfactory.

Thermal analysis traces for sludge and laboratory grade $Cu_2(OH)AsO_4$ were obtained at 10 °C.min^{-1} in flowing air [Figs. 2.2, 2.3]. While they appear to be gaining weight past 400 °C, this is actually an increase in buoyancy arising from the heating of the gas stream. The effect is roughly linear and can safely be subtracted.

Sludge appears to lose physisorbed water around 100 °C. The copper arsenate exhibits a sharp loss at 400 °C, involving the hydroxide groups, which is clearly not shared by sludge. It only shows a gradual loss up to that temperature, which must involve decomposition of organic material as well as loss of chemisorbed water, for there is a slight difference when the experiment is run in OFN [Figs. 2.4, 2.5].

The next weight loss phase appears much earlier in OFN than in air. So the volatilisation must be reductive, and it probably involves arsenic species since a similar event occurs at higher temperatures in the copper arsenate. Plausible processes include

$$AsO_4^{3-} \longrightarrow AsO_2^- + O_{2(g)} + 2e^-$$

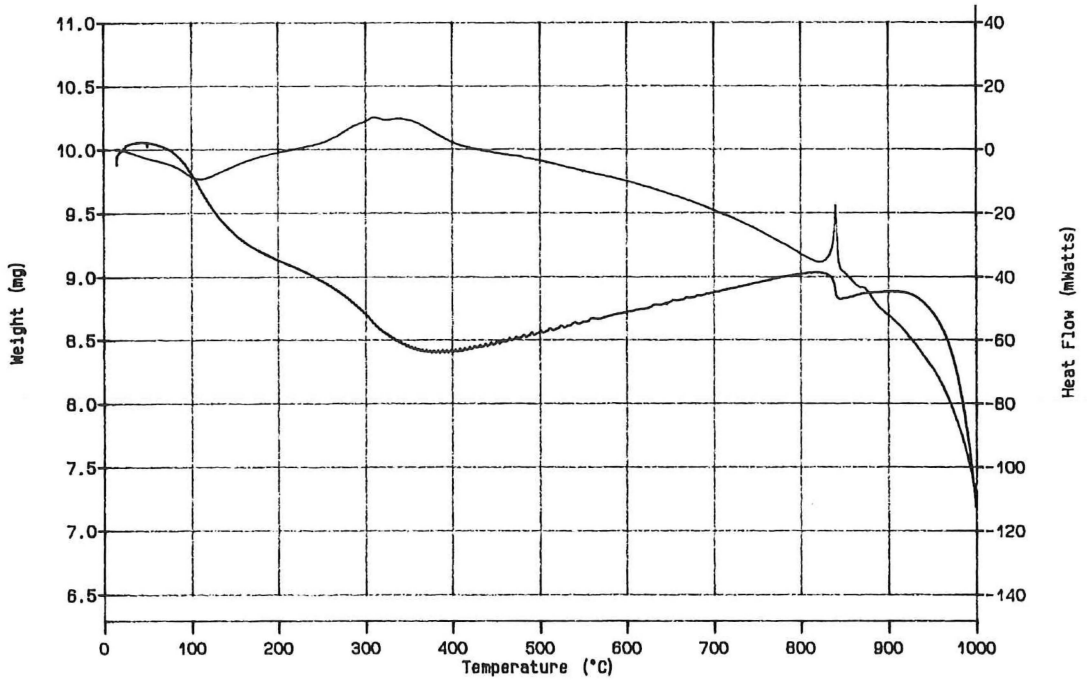
$$AsO_2^- + 2e^- \longrightarrow As^{3-} + O_{2(g)}$$

$$4AsO_2^- \longrightarrow As_4O_{6(g)} + 2O^{2-}$$

There is no indication of As^{III}, which is relatively volatile, in the original material. Also, cuprous compounds are more stable than cupric at high temperature, which can lead to mass loss. For example,

$$2CuCl_2 \xrightarrow{300°} 2CuCl + Cl_{2(g)}$$

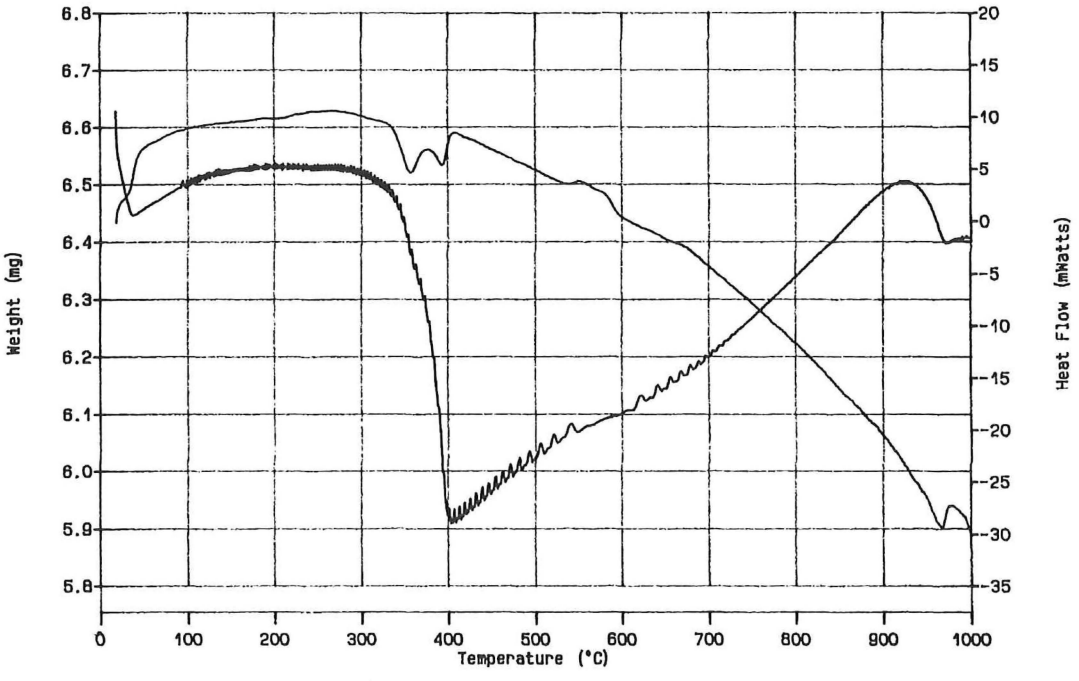
Figure 2.2



Sludge in flowing air

Upper curve: heat flow Lower curve: weight

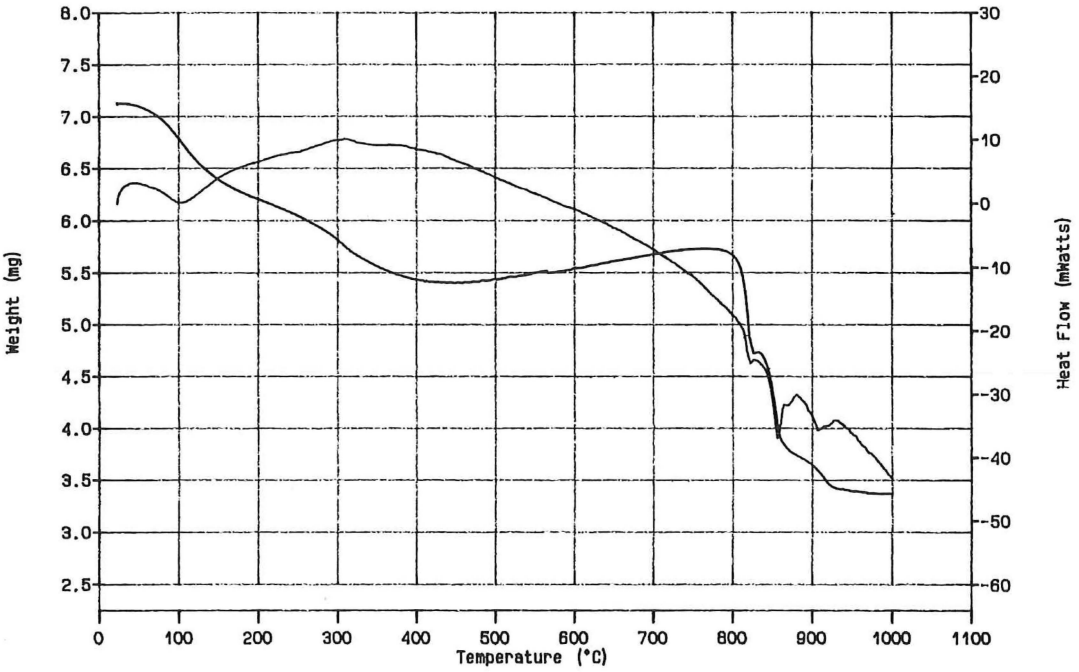
Figure 2.3



$Cu_2(OH)AsO_4$ in flowing air

Upper curve: heat flow Lower curve: weight

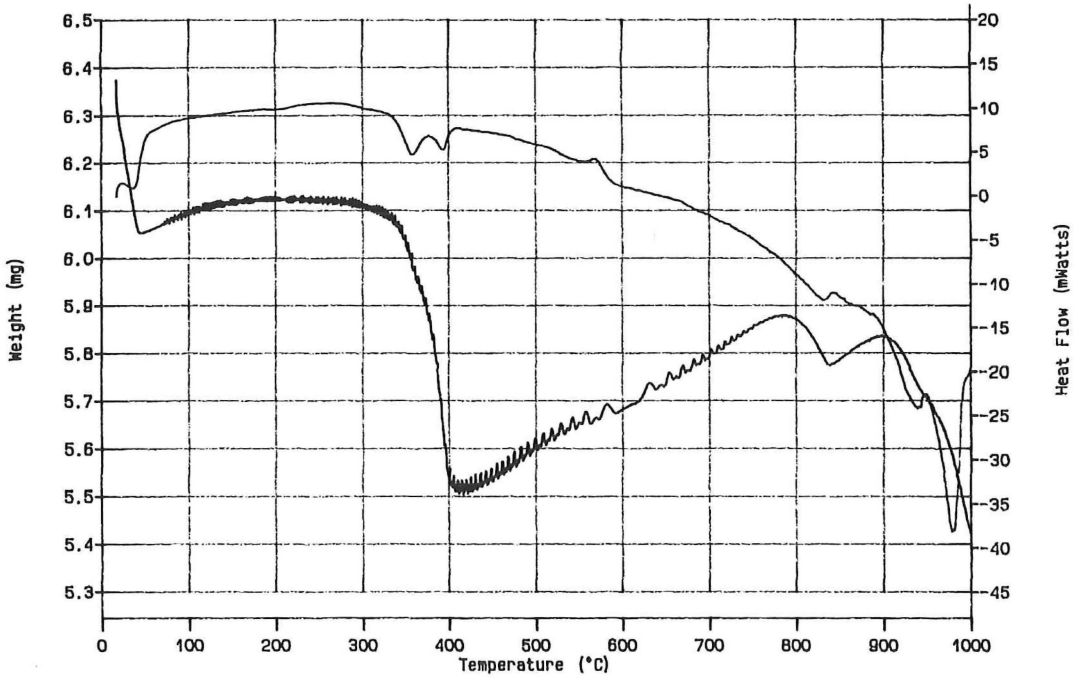
Figure 2.4



Sludge in O_2-free N_2

Upper curve: heat flow Lower curve: weight

Figure 2.5



$Cu_2(OH)AsO_4$ in O_2-free N_2

Upper curve: heat flow Lower curve:weight

The 900 °C residue was identified above as Cr_2O_3 and $NaNiCr_2(AsO_4)_3$. Since there is no nickel in sludge, the latter component must be the equivalent copper material $NaCuCr_2(AsO_4)_3$. If the residue after firing contains only three As for each Cu, then a little over half the arsenic has been lost. Calculated as As_2O_5, that is a mass loss of about 22%, roughly the same as the two steps down to 850 °C in the sludge/OFN TGA. This is consistent with the conversion of $CrAsO_4$ to Cr_2O_3, O_2, and As_4O_6.

A number of workers have reported that most but not all of the arsenic content is volatilised when CCA-treated wood is burnt. Dobbs and Grant[13] volatilised an average of 20% at temperatures of 840- 960 °C, 60% in oxygen-enriched air at over 1100 °C. The results of M^{c}Mahon et al.[14] are higher but perhaps less reliable. Dobbs and Grant have excellent mass balances and volatilise no chromium or copper from the ash, whereas M^{c}Mahon et al. volatilise around 10%; plausibly they evolved particulate matter containing unburnt arsenic. A close inspection of the experimental procedures reveals that, unlike Dobbs and Grant, they had no plug to prevent this happening. Their observation of arsenic losses at 400 °C may be an unfortunate artifact of this effect. More recent results by Pasek and McIntyre[15] suggest that volatilisation begins at around 600 °C. However, their mass balances were substantially poorer yet, particularly at high temperatures where calcination made the residues insoluble, hence hard to analyze. All three groups used Pinus species treated with similar formulations of CCA, so there was no reason for different results.

Here it seems that the proposed $NaCuCr_2(AsO_4)_3$ is more thermally stable than $CrAsO_4$, since $NaCuCr_2(AsO_4)_3$ and Cr_2O_3 account for the observed XRD pattern and there is no sign of the background hump produced by amorphous $CrAsO_4$. This may be the reason for the observed partial losses of arsenic from treated wood. If $CrAsO_4$ decomposes above 600 °C to give $Cr_2O_{3(s)}$ and $As_2O_{3(g)}$, while copper-containing arsenates do not decompose until over 900 °C, perhaps to products including refractory copper arsenides, that might just account for the observations. More work in this direction seems imperative. Unfortunately costs were becoming prohibitive for this project.

UVA of sludge solution and chromic sulfate are shown in Figure 2.6. The intense greenish-black colour of the concentrate implies extensive oligomerisation of the chromium (III) complexes[16]. This is consistent with the slight increase in ε and λ_{opt} relative to the standard hexaquochromium (III) ion on dilution[17]. However, the difference is not great, so there may be considerable dissociation. There is no sign of any chromium (VI) peak, which would be centred on 350 nm, nor of any highly coloured copper species.

FTIR fingerprints of sludge and pure $CrAsO_4$, as KBr disks, are shown in Figure 2.7. These spectra are consistent with those obtained by Michell[18]. The peaks centred on 490 and 850 cm^{-1} are characteristic of AsO_4^{3-} but could include other MO_4 ions such as SO_4^{2-}, and CrO_4^{2-}; the peaks at 3150 and 1617 indicate water, but could include hydroxide groups. The weak group around 1060 is consistent with sugars or sulfate. Again, there is no sign of arsenic (III).

Figure 2.6 UVA spectra of sludge solution and chromic sulfate

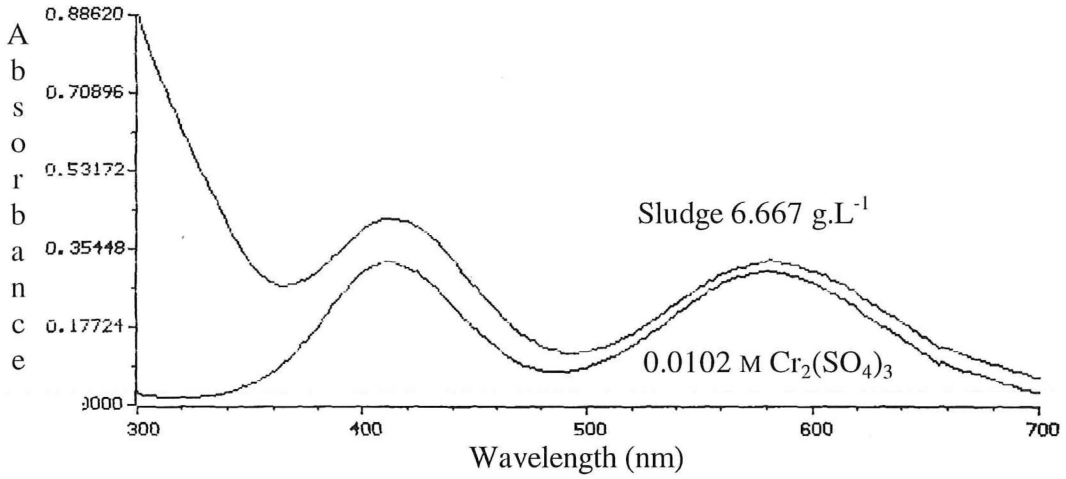
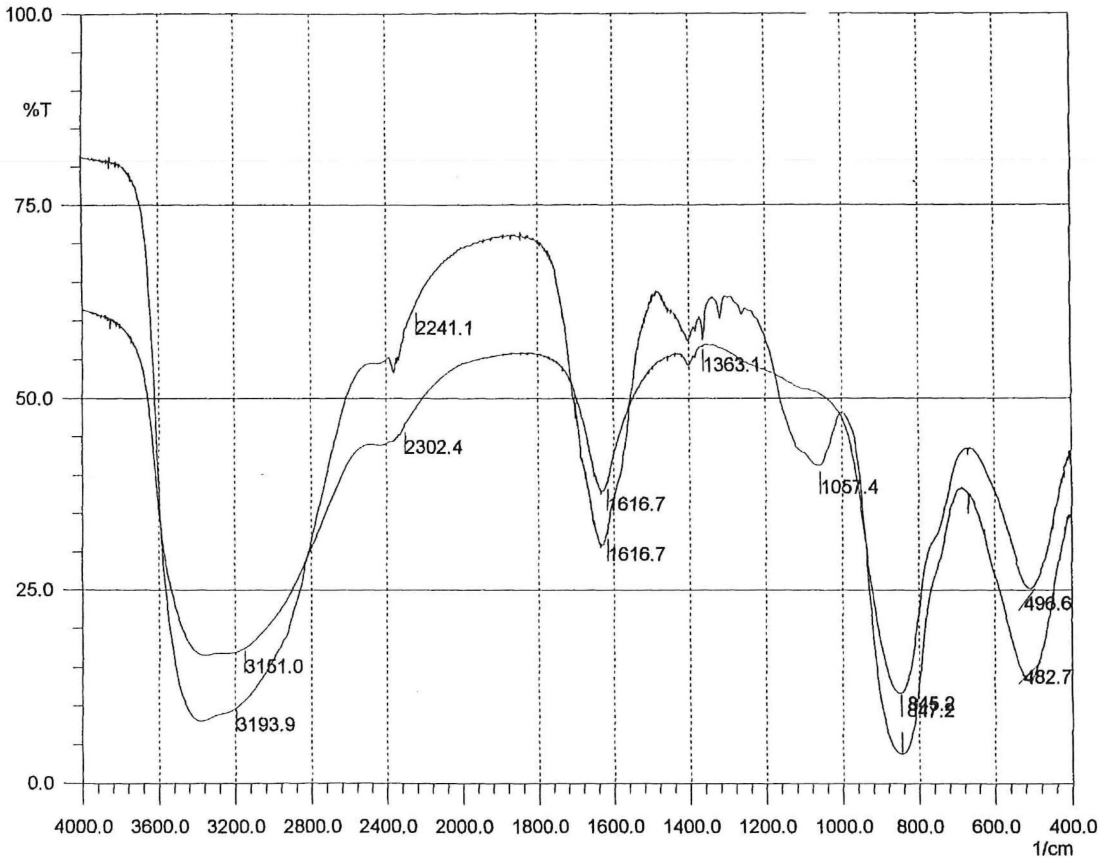


Figure 2.7 FTIR spectra of sludge and chromic arsenate



(The sludge spectrum has the peak at 1057 cm^{-1})

The ill-defined green polymeric form of pure chromic arsenate has been described by a number of authors[19,20,21,22]. The results presented here are generally consistent with those studies, especially when comparisons with the infrared and thermogravimetric spectra of the violet-grey $[Cr(H_2O)_6]AsO_4$ form are included.

However, there is no evidence here to support any large proportion of OH^- and corresponding $HAsO_4^-$ groups as proposed by Lukaszewski *et al.*[21]. Further, the substantial fraction of copper cannot be accounted for in terms of the weak cation-exchange properties demonstrated by Lukaszewski and Redfern[22]. The difference may lie in the preparation; Lukaszewski and Redfern exposed a pure chromic arsenate solid to $CuSO_4$ solution, but sludge forms in the presence of Cu^{II} and surely has much greater opportunity for uptake of copper, or of hydrogen ion which could be exchanged for Cu^{2+}.

The minor constituents can readily be substituted into such a structure. Fe^{3+} is very similar to Cr^{3+} and is well known to coprecipitate at low pH[23]. Similarly phosphate may substitute preferentially for arsenate[24]. In contrast, while silicates could fit into such a chemical structure, it is more likely that they come from dust particles that were suspended in solution.

The organic fraction appears to be dominated by carbohydrates, but may contain a wide range of wood extractives. Unfortunately, this sludge arises from many treatments of a single species of softwood, and nothing is now known about sap content, etc., of any of that timber. Since there is no reason to suppose the organic fraction will remain constant from time to time, let alone for different species, there is no basis here for generalising about either its proportion or its composition.

Apart from the organic fraction, the only significant contaminants are quarter of a percent each of iron and antimony. Thus, this sludge is surprisingly pure, meaning it has considerable potential as a CCA raw material if the chromium (III) can be removed. The iron may have come from treatment plant corrosion, or from preservative raw materials where it is a typical trace contaminant. While iron is known to have detrimental effects on CCA[25], the low level found here suggests that preservative quality was not a significant cause of sludging in this case.

The sludging process

In a simple experiment, sludge solutions were adjusted to various pH until the point of reprecipitation could be bracketed. Most reprecipitation occurred within minutes, but it was observed to continue for over a week. During sludging, the pH decreased, but never to less than the value at which solutions became unstable.

Sludge solution was prepared by dissolving 100g of the standard sludge in the minimum volume (150mL) of hot 20% H_2SO_4. The cooled solution was vacuum filtered and made up to 500 mL with distilled water. Aliquots were diluted to 20 gL^{-1} and varying amounts of 5.00M NaOH were added dropwise while stirring and monitoring with a Cyberscan 20 pH meter, accurate to within ± 0.05 units. The aliquots were stored in sealed glass containers for one month and then a final pH measurement was made. Further aliquots were briefly heated to boiling point after pH adjustment, or made to 2% with fresh CCA, or made to 0.7 gL^{-1} iron (III) as the chloride; then allowed to cool and stored in the same way. The 'final' measurement of pH was made some weeks later, after which time it remained constant.

Table 2.7 pH dependence of sludging

Solution	Original pH	Final pH	Sludging
Sludge	>3.5	2.75	complete
	2.85	2.5	yes
	2.5	2.25	yes
	2.25	2.3	no
	2.0	2.05	no
	1.5	1.6	no
Sludge and iron	2.5	2.2	yes
	2.25	2.1	yes
	2.0	1.85	yes
	1.7	1.65	no
Sludge in CCA	2.5	2.3	yes
	2.3	2.2	trace
Sludge, boiled	2.3	2.3	yes
	2.1	2.1	trace

The sludges from iron-doped solution were paler, but still visibly chromic.

It appears that there is a sharply defined critical pH for precipitation. In this experiment, sludge solution was seen to reprecipitate between pH 2.25 and 2.30. For CCA, Mutandadzi and Evans[5] observed a critical value of 2.34, and Hartford reported sludging between 2.30 and 2.50, or 1.85 in the presence of iron (III)[25]. Heating should increase the relative rate of condensation, and indeed the critical pH appears to be substantially less in heated sludge solution. This is probably a principal cause of the increase in sludging at high ambient temperature[25].

While the first pK_a of free arsenic acid is 2.25, very close to the critical pH for sludging, there is no mechanistic reason to connect the two. Free arsenic acid may exist in bulk CCA, but in sludge solution all arsenate should be complexed to chromium, which will change its hydrogen ion affinity. Anyway, iron (III) arsenate presumably forms by a similar mechanism, but its critical pH is at least 0.5 units lower.

The sludging process appears analogous to behaviour observed in the chromium (III)-hydroxide system. When solutions of $[Cr(OH_2)_6]^{3+}$ are aged in increasingly basic conditions, stable chromic hydroxide oligomers begin to form[16,17]. Dimers, trimers, tetramers, and hexamers have all been observed, even highly condensed polynuclear species like $[Cr_{12}(OH)_{28}(H_2O)_{12}]^{8+}$. Chromium (III) is kinetically inert in solution, so the aging process can take years to reach equilibrium. Surprisingly, oligomers can be rendered relatively labile by deprotonation; for example,

$$monomer^{2+} + monomer^{2+} \xrightarrow{k=2\,M^{-1}s^{-1}} dimer$$

$$monomer^{+} + monomer^{2+} \xrightarrow{k=3800\,M^{-1}s^{-1}} dimer$$

Likewise, increasing pH should minimise acid cleavage of polynuclear $CrAsO_4$ species, allowing higher and higher oligomers to form. At the same time, the chromium (III) will become more labile, so the rate of oligomerisation will increase. Large condensates will form, then particulates, and finally the polymeric solid will precipitate out. It is no surprise that the aging process takes several days in bulk solution, for the strong buffering action of arsenic and chromic acids will keep pH changes to a minimum. The observed decrease in pH during reprecipitation of sludge solutions, and the apparent absence of H^+ in well aged sludge, suggests that the condensation reaction itself releases H^+.

Dahlgren and Hartford[2] deduced from pH measurements and basic principles that a Lukaszewski-type compound, formalised as

$$H_m Cu_n Cr_{3-m-2n/3} AsO_4$$

was originally formed during fixation, then slowly converted to their final products;

$$\longrightarrow \tfrac{3-m-2n}{3} CrAsO_4 + \tfrac{n}{2} Cu_2(OH)AsO_4 + \tfrac{2m+n}{6} H_3AsO_4$$

The release of arsenic acid, which of course is freely soluble, would account for the decrease in pH during the aging process. Actually, the structure proposed by Lukaszewski et al. themselves was

$$Cr_2(OH)\left(ZAsO_4\right)AsO_4; \quad Z \in H^+, K^+, \tfrac{1}{2}Cu^{2+}$$

which only underwent weak ion-exchange, not disproportionation. Oligomerisation processes appear to better account for the observations.

In any case, there is no evidence in the DTA or elsewhere for any large proportion of hydroxide groups, which would be necessary for free $Cu_2(OH)AsO_4$, or the Lukaszewski structure for chromic arsenate; or indeed for the equivalent number of replaceable hydrogen ions which would be required to balance them out.

It must not be concluded that sludge should be controlled by *ad hoc* pH adjustment. Though Kuppusamy and Sharma[26] demonstrated that sludging could be eliminated by adding sulfuric acid after treatment, even a small amount of acid will increase corrosivity of the solution, dramatically impair fixation, and weaken the timber product [Ch. 3]. Chemical modification of CCA with chelating agents or buffers is inadvisable because they should inhibit fixation reactions just as effectively. Citrate seems particularly unsuitable since it is a powerful leaching agent for CCA[27,28,29].

These results are consistent with a simple model for green sludge; an impure, amorphous chromic arsenate, roughly tetrahydrate, $[Cr,M]AsO_4 \cdot 3.7H_2O$. The formation process is pH-dependent, oligomers condense into the polymeric solid above a critical pH of 2.3, or less at elevated temperature.

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3 Returning treatment plant sludges to process

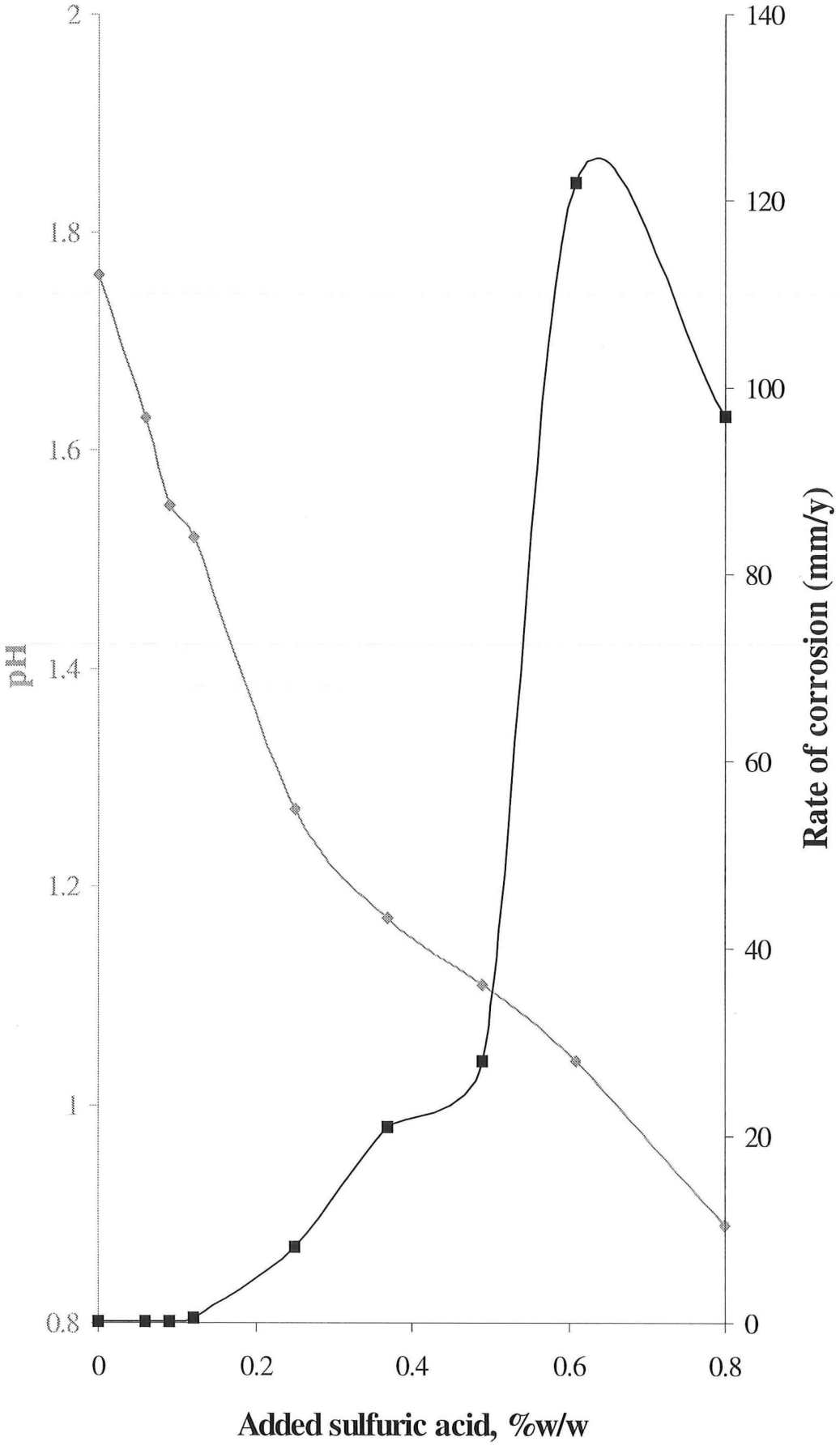
Since timber treatment plant chemical sludge is rich in arsenic (V) and soluble in strong acid [Ch. 2], it might be possible to use it in the CCA manufacturing process. Butler[1] developed a mobile sludge recycling system on this principle which is no longer in operation. According to a former colleague of his, Jack Norton of the Queensland Forest Research Service, it became unprofitable. It has also been alleged that use of unwise quantities of acid caused corrosion damage in customer plant. Such problems have been reported elsewhere[2]. Certainly there are a number of concerns about the viability of acid solubilisation, and the fate of sludge chromium (III) and minor contaminants.

Steel can be corroded by reaction of copper (II) with iron, particularly when activated by acidity, sulfate, or other anions such as chloride. As well as destroying the plant, this increases the iron concentration and hence causes sludging [Ch. 2]. In CCA this is prevented by chromium (VI), which is a strong anodic corrosion inhibitor at low temperature[2]. But this protection will be nullified by relatively small additions of sulfuric acid. Fox *et al.*[3] found that the corrosivity of 2% CCA to carbon steel increased rapidly with increasing sulfuric acid concentration [Fig. 3.1]. Just as importantly, they found that high sulfuric acid levels interfered with fixation, increasing copper leachability and leading to premature failure in field tests.

Thus it is important to use a minimal amount of acid. A simple experiment here showed that one kilogram of sludge solids will dissolve in only 0.3L of 98% sulfuric acid, diluted in several volumes of water and boiled. This corresponds to three sulfuric acid molecules for each two arsenate ions, or one stoichiometric equivalent with respect to protonation. Exothermic hydrolysis of the acid will provide much of the necessary heat. At lower temperatures, more acid is necessary to dissolve substantial amounts of the sludge, even over several hours[4].

Sulfuric acid also causes a sticky, brownish-black solid to form, accompanied by a caramel odour. This intractable material is probably based on polymerised carbohydrates [Ch. 2]. It is a terrible filter medium, and insoluble in a variety of solvents including water. It can be handled easily enough in the laboratory, but filtration on an industrial scale would be impractical. Other possible constituents include undissolved sludge, lead and antimony compounds, particulate matter, etc., so it can be expected to require equally careful and expensive disposal. Reactions between organic material and acids can also cause excessive foaming when sludge is incorporated into production streams.

Figure 3.1 Corrosivity of CCA with increasing $[H_2SO_4]$ [3]



Chromic and arsenic acids are potential alternatives to sulfuric acid. They would not introduce extra salts into CCA, and they do not activate corrosion in the same way. But a five-fold excess of boiling 20% arsenic acid takes some hours to dissolve sludge, although the precipitate is less caramelised and thus easier to handle than that generated by sulfuric acid. It might also contain iron and lead arsenates which should be insoluble under these conditions. According to FTP sources, this emerald green solution has been used in arsenic acid production, where the nitric acid reagent is able to destroy the organics, but there were problems with foaming. Chromic acid is equally slow to act, and it has been reported that chromic acid solutions of sludge are not particularly stable[1]. Further, the organic material in sludge is still able to reduce chromium (VI) when mobilized[4]; it would be a waste to add chromic acid until polymerisation was well advanced. Butler obtained "optimum results" with successive additions of 40% chromic acid and 98% sulfuric acid to dewatered sludge[1], although he does not state what criteria were used to determine that optimum.

It is rare for more than 5% of preservative to end up as sludge. Treaters processing unseasoned hardwoods in tropical conditions, such as Butler's Queensland customers, might well reach that level. Most treatment operations should generate rather less. Therefore, to 'close the loop' by reintroducing solubilised sludge to preservative, it should not be necessary to exceed one part by weight of sludge solids to twenty parts preservative salts.

The New Zealand Timber Preservation Council's standard for the usual type 1 CCA[5] requires the preservative to be composed of 23-25% copper (II), 43-47% chromium (VI), and 30-32% arsenic (V). Addition of the sludge characterised in Ch. 2 at a level of one part solubilised chromium (III) per twenty parts chromium (VI) would contribute more iron, lead, and antimony than all the other raw materials put together, assuming quality control requirements similar to those at FTP. The maximum total for a 20% preservative solution would still be below the 100 ppm combined limit for iron and lead recommended by the American Wood-Preservers' Association[2]. But there is no guarantee that any other sludge would meet these guidelines. Also, if the sludge had been solubilised with the minimum amount of sulfuric acid, the sulfate concentration would be increased by about 18%. Thus, it is unlikely that added free acid would exceed 0.01% by weight of a 3% preservative solution. Again, no ill effect should result.

Fresh CCA concentrate was modified with sludge solution at a level of one part chromium (III) per twenty parts chromium (VI), including sufficient sodium dichromate and copper sulfate to ensure the CCA elements were in the correct proportion. It was then diluted with factory water so as to make 100L of 3% working solution. There was no reprecipitation on standing for several days nor on dilution to 1% CCA. Further fresh concentrate was diluted to the same extent with the same water. Both solutions had a pH of 2.0. The modified solution was markedly off colour, especially before dilution, and FTP opinion was that customers would not be interested in it for that reason. Nonetheless, these solutions were then used in pressure treatment experiments.

FTP's 80L test unit was designed to mimic industrial conditions on a relatively small scale. In each experiment the cylinder was packed with 14 individually weighed 1 metre lengths of steamed rough sawn 50×75 *Pinus radiata* timber without major defects or large sap deposits on the surface, obtained from Tuakau Timber Treatment Ltd.. The moisture content was approximately 15%, determined by drying sample sections at 105 °C overnight. Each treatment consisted of 20 alternating pressure cycles; ramping up to between 1300 and 1400 kPa over roughly 50 seconds, holding for 2 minutes, and returning to ambient pressure over a minute or so. The work solution was continually recirculated, debris being kept out of the bulk solution by a 1 μm polypropylene bag filter placed over the end of the cylinder exit hose; this did not trap any chemical sludge in either experiment.

An alternating pressure treatment was chosen to maximise the potential for sludging, highlighting any significant difference between the two solutions. APM encourages 'kickback', the expansion of air trapped within the wood which expels reacting CCA from the wood back into the bulk solution. This extract is acid deficient, and rich in wood extractives and reduced chromium, all causes of sludging. Steamed timber and minimal solution volumes should have aggravated the situation further. However, the desired CCA retention was only 12 $kg.m^{-3}$. This would put the timber in hazard class H4, suitable for ground contact uses. In New Zealand, H4 is the most common CCA treatment grade.

The day after treatment, both solutions had a pH of 2.2. XRF analysis using FTP's standard quality control technique gave the following results;

Table 3.1 Used work solutions by XRF

% w/w	Standard	Modified	Fresh CCA
Cr	0.449 ± 0.016	0.469 ± 0.022	0.477
Cu	0.237 ± 0.006	0.241 ± 0.004	0.256
As	0.298 ± 0.006	0.307 ± 0.004	0.329
Total	0.984 ± 0.02	1.017 ± 0.03	1.062
Strength	2.78 ± 0.06	2.87 ± 0.09	3.00
ΔV (L)	18.3 ± 1.4	23.0 ± 1.3	
Retention (kgm^{-3})	13.7 ± 0.8	15.0 ± 1.1	

The observed changes in solution volume were 18.3 ± 1.4 and 23.0 ± 1.3 L respectively, implying actual retentions of 13.7 ± 0.8 and 15.0 ± 1.1 kgm^{-3} respectively. The large error is mostly derived from the chromium analysis. At the time, the aging Asoma 8620 used in the quality control laboratory had problems with chromium, which were later tracked down to an electronic design fault. A standard titrimetric technique[6] was used instead, total chromium also being determined after oxidation of the chromium (III) content by sodium persulfate;

Table 3.2 Used work solutions by titration

	Standard	Modified
Chromium (VI), %w/v	2.75 ± 0.02	2.66 ± 0.02
Total chromium, %w/v	2.77 ± 0.02	2.86 ± 0.02
Chromium (III), %w/v	0.02 ± 0.04	0.20 ± 0.04
Proportion chromium (III), %	0.7 ± 1.5	7.5 ± 1.6

Using these more accurate figures, the retentions become 14.3 ± 0.6 and 15.6 ± 0.8 kgm^{-3}. Chromium (III) discoloration was clearly visible in both solutions. Since the modified solution originally contained an extra 5% chromium (III), and now contains 4-8% more than the standard solution, it does not seem that the reduced chromium has been taken up preferentially [cf. Ch. 7]. If solution pH ever went over the critical limit, not only would the sludge have been regenerated, but some additional material might form as well.

The timber was left in the open cylinder overnight to drip, then removed and left to air dry. The two heaviest and two lightest blocks were discarded, then six of the remainder were selected arbitrarily for further analysis. A cross-section *ca.* 1 cm across was cut from a different point along each, never within 5 cm of an end. These slices of wood were broken up, run twice through a flour mill, dried at 60 °C, and the resulting sawdusts combined. Six weighed subsamples of each were analysed with the same XRF spectrometer as above. Average Cr:Cu:As weight ratios of 1.26:0.65:1 were obtained for the standard, 1.19:0.57:1 for the modified treatment, which therefore appears to be high in arsenic. There is no basis for comparing absolute percentages, which were dependent on sample density, etc..

Each sawdust was leached for three months in sealed jars, 10 g to 200 mL of 0.1M acetate buffer solution, pH 4, as used in the United States Environmental Protection Agency's Toxicity Characteristic Leaching Protocol test. This test was substantially longer than a TCLP, in order to magnify any difference between the two, though properly fixed wood should not exhibit significant leaching under these mild conditions [Ch. 1]. Neither solution showed any chromate colour on oxidation with persulfate, so there must have been less than 5 ppm chromium in the leachates. This was considered to be within acceptable levels; without immediate access to any other form of instrumental analysis, the exact trace levels were not determined.

Low level reintroduction passes elementary tests of solution stability and fixation. The only observed effect was a slight relative increase in fixed arsenate. However, spent chromium does not appear to be consumed during treatment, and therefore it seems most unwise to reintroduce without reoxidation. Very small quantities of sludge might conveniently be disposed of in arsenic acid production.

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4 Chemical extraction

The presence of spent chromium (III) appears to be the chief barrier to reusing CCA wastes. It seemed sensible to consider a selective chemical extraction agent. Either chromium (III), or else all the other components, have to be rendered insoluble or extractable. Any practical extractant must be compatible with CCA components, and must be recoverable unless it is very cheap.

Ion exchange techniques are an obvious alternative, particularly since they have been used with some excess in cleaning up tanning wastes containing chromium (III). However, they do not seem tenable in this context. It appears that chromium (III) remains strongly bound to arsenate when sludges are dissolved in strong acid [Ch. 2, 5], which would make it difficult to separate chromium from arsenic. Further, such solutions contain massive amounts of the target species and appreciable concentrations of a wide variety of inorganic and organic contaminants; it seemed highly probable that chromium-selective membranes or columns would be rapidly poisoned. Significant dilution is not practicable on an industrial scale.

The classic analytical method for extracting chromium (III)[1] uses acetylacetone (2,4-pentanedione), a chelating agent for many metal ions. Acetylacetonates are so soluble in organic solvents that the method is applicable on a macro scale. The chromium (III) complex can be selectively extracted because it forms so slowly. Other metals are removed in a first extraction, then the solution is neutralised and extracted again under reflux for an hour. Unfortunately the chromium (III) complex is extremely stable in the organic phase, preventing back-extraction even at very high acidity. Worse, the pH required for extraction is a long way above the critical value for chromium (III) arsenate precipitation [Ch. 2].

A literature search turned up several interesting alternatives. Beneitez and Ayllon[2] had some success in extracting chromium (III) from acid media into kerosene with bis(2-ethylhexyl)phosphoric acid. Sulfate inhibited the extraction considerably, so it seemed likely that arsenate would be extremely detrimental. Ohki *et al.*[3] reported that trioctylphosphine oxide "TOPO" was more effective, but their method actually involves extraction of chromium (VI), which is then photo-reduced to chromium (III) in order to back-extract from the toluene phase. Nonetheless, TOPO does extract iron (III) from strongly acid solutions into cyclohexane[1]. A simple experiment showed that cyclohexane containing TOPO became yellow-green when shaken with sludge dissolved in minimal amounts of strong mineral acid. However, TOPO is a severe irritant, and very toxic to aquatic organisms, according to hazard data from the manufacturer. Therefore, it was considered unsuitable for large scale environmental work.

Heptafluorobutanoic acid "HFBA" in ether can separate trivalent cations from most divalent or monovalent cations.[4] Unfortunately, even fluoride and sulfate prevent extraction, so a strongly coordinating anion like arsenate will certainly do so.

Hon and Chang[5] allege that guaiacol (2-methoxyphenol) forms complexes with chromium which are poorly soluble in water but include an organic soluble fraction. There seems to be some confusion in the article as to the chromium oxidation state, possibly because their reagent, chromic acid, does not contain chromic ions! It appears from the observed increase in pH that reduction to chromium (III) took place. Therefore guaiacol was oxidised, which would form *o*-benzoquinone, muconic acid (hexa-2,4-dienedicarboxylic acid) and formic acid [Ch. 7]. FTIR and UVA should have been able to settle the question, but the relevant regions are not shown in their published spectra. On the whole, the report was considered somewhat equivocal, and since carboxylates were not promising extractants[1,2,4] no experiments were carried out.

Donaldson and Mark[6] reported that ethylxanthate, $EtOCS_2^-$, could extract copper and arsenic, but not chromium (III), from sulfuric acid media. Copper (II) reacts to form a poorly soluble copper (I) complex, while arsenic (III) and some proportion of the arsenic (V) are chloroform-extractable. Since ethylxanthate is readily prepared from cheap materials, this reagent appeared ideal.

O-ethylcarbonodithioic acid potassium salt, "potassium ethylxanthate", was synthesised in the same manner as described in the literature[7]. A known amount of potassium hydroxide was completely dissolved in hot ethanol, and one equivalent of carbon disulfide was added to the cooled solution. The precipitating mixture was cooled on ice, filtered, and washed with ether. The product could be recrystallised from ethanol. The FTIR and ^{13}C-NMR spectra of the crystalline material appeared consistent, although the carbon atom in the xanthate functionality was not visible, presumably due to extensive coupling with the sulfur atoms. No other carbon signals were visible.

The presence of undissolved KOH leads to a reddish orange impurity in the product, probably potassium dithiocarbonate. The presence of excess water seems to aggravate this tendency. Thus the synthesis of O-octylcarbonodithioic acid potassium salt, potassium octylxanthate, included a separation step to remove the water layer before carbon disulfide was added. KOH was significantly less soluble in octanol, which translated into a reaction yield somewhat smaller than expected.

Chromic ethylxanthate was prepared by the addition of KS_2COEt to a strong aqueous solution of $CrK(SO_4)_3 \cdot 12H_2O$, which when shaken with chloroform yielded a green precipitate and a small amount of purplish blue organic-soluble material, crystallising as purple needles on separation. Cuprous xanthates were prepared from addition of excess KS_2COEt or $KS_2COC_8H_{17}$ to strong aqueous $CuSO_4 \cdot 5H_2O$, immediately yielding a yellow amorphous solid which would not dissolve in reasonable amounts of a wide variety of solvents. Arsenous ethylxanthate was prepared from addition of excess KS_2COEt to $NaAsO_2$ in ca. 0.2M H_2SO_4, immediately yielding a white powder which was extremely soluble in chloroform.

However, a number of problems presented themselves. Xanthates are quite basic, rapid addition to sludge solutions simply resulted in reprecipitation. Xanthic acids are not thermally stable, so heating to accelerate the slow chromium (III) kinetics is not an option. Being thio compounds, they oxidise readily, reducing copper (II) and probably arsenic (V)[6,8]. Xanthates have a foul and penetrating odour, and one starting material, carbon disulfide, is carcinogenic. Slow addition of xanthates to sludge solution immediately precipitates the copper (I) compound. The cuprous ethylxanthate is practically insoluble in a wide variety of solvents, and is almost impossible to remove from glassware, especially ground glass joints or sintered glass filters.

Octylxanthate was synthesised in the hope that the longer side chain would increase the solubility of the copper complex, which turned out to be the case. Further, octanol is insoluble in water, offering the possibility of a one pot synthesis and extraction so long as chromium (VI) is not present. Both the copper (I) and arsenic octylxanthates were expected to move into the alcohol phase, from whence they could be extracted and reoxidised.

Neither xanthate showed any enthusiasm for reaction with chromic arsenate in cool solution. The oligomers probably present too much of a steric hindrance, not to mention the usual chromium (III) kinetic considerations [Ch. 2, Ch. 5]. Excessive dilution would probably help but is impractical.

At this stage, Prof. D.A. House suggested that chromic arsenate might be soluble in strong base. That would open up the possibility of extraction under radically different conditions, where the chromium (III) would be more labile and would not have to compete with hydrogen ion for extractants. Accordingly, sludge was added to 2 M sodium hydroxide. It gradually dissolved to give a dark green solution, similar to the acid sludge solutions [Ch. 2] though not as intensely coloured. On heating, the solid appeared to reprecipitate, the green colour completely disappearing from solution overnight. Though the product was visually identical to the original sludge, a FTIR fingerprint indicated that it was radically different, probably chromic hydroxide. ICP-OES analysis was performed by Campbell Microanalytical Laboratories [cf. Ch. 2] and an astonishing result was obtained:

Table 4.1 Hydroxide extraction product

%w/w	Sludge	Precipitate
As	**25.5**	**0.52**
Cr	16.0	13.2
Cu	3.2	7.0
Na	0.97	3.0

Hydroxide alone had achieved a remarkably effective separation of arsenic!

In hindsight, perhaps this approach should have been tried earlier. The inorganic chemistry literature not only showed that excess base would keep chromic hydroxide in solution, but was engaged in an argument as to whether the 'chromite' anion $Cr(OH)_4^-$ existed[9].

Further experiments showed that the hydroxide precipitated completely over time, almost immediately if boiled or overnight if left to stand. The supernatant was a yellow-brown colour, apparently organic material. If a threefold excess of at least 4 M sodium hydroxide was used for the separation, the supernatant would condense into an ugly gelatinous material on standing. Low volumes also led to the formation of massive clusters of rod-shaped colourless sodium arsenate crystals. A UVA spectrum of this supernatant showed peaks at 258 nm and 360 nm. Therefore the colour is not due to the Maillard products identified in hot water extracts of *P. radiata* by McDonald *et al.*[10], since those compounds had peaks at 220 and 280 nm; nor to lignin or stilbenes which would be expected to give peaks at around 300 nm. A deprotonated lignin derivative, perhaps a hydroxyphenolate, is one possibility. Unfortunately no positive identification could be made, due to the relatively low concentration of organic material. ^{13}C NMR, FTIR, and fast atom bombardment mass spectrometry all gave inconclusive results.

The reaction appears to work with a relatively small excess of hydroxide. A subsequent extraction with 20% excess gave a precipitate containing 0.7% As, according to the same analysts. 3.0% C was also found, representing about half the organic content of the original sludge [Ch. 2]. Therefore the remaining half must be retained in the supernatant.

The arsenate value can be isolated by adding the supernatant dropwise to stirred copper sulfate solution. A blue powder is formed, analysing as 29.4% As, 30.0% Cu, 0.3% C (Campbell Microanalytical Laboratories, cf. Ch. 2). This does not correspond to a simple cupric arsenate, but may be the $Cu_3(AsO_4)_2{\cdot}2CuHAsO_4{\cdot}9H_2O$ reported by Más and cited in Dahlgren and Hartford[11], which would be 28.88% As, 30.62% Cu. Such a compound could readily be used in the manufacture of oxide formulations of CCA. Alternatively, the supernatant could be acidified with chromic or arsenic acid, and used in the manufacture of CCA salt. The use of chromic acid does impose a further cost, since it is more expensive per unit of chromium than the sodium dichromate normally used in salt formulations.

A 3% solution of CCA salt was made from supernatant, chromic acid, copper oxide, and sulfuric acid, such that the arsenic content arose solely from sludge extracts and the CCA met the usual FTP quality control requirements. No discolouration or precipitation was observed on simmering for an hour, followed by three days standing at room temperature. Hence, any remaining contaminants pose no threat to solution stability.

There are drawbacks to this approach. The copper component of the sludge is not extracted, though this is forgivable since it only amounts to 3% [Ch. 2]. More importantly, without a recycling process for the precipitate, the total amount of chemical waste has not been reduced significantly. A method for oxidising chromium, or an alternative consumer of the hydroxide, is still necessary.

Several months after this discovery, Kazi and Cooper[12] showed that excess 10% sodium hydroxide could leach out 91% of the arsenic yet only 18% of the chromium from CCA-treated wood. They ascribe this to the fact that arsenate is soluble in base, whereas uncomplexed chromium (III) is not. However, it should now be clear that such explanations are inadequate. The arsenic component of treated wood is probably dominated by chromium (III) arsenate [Ch. 7]; this will be briefly solubilised by strong base, but chromium hydroxide will reprecipitate following base hydrolysis and aging. Hence, presumably, the release of a small part of the chromium.

It should also be noted that Pasek and M^{c}Intyre extracted a considerable proportion of the copper from CCA contaminated soil using ammonia solution[13], presumably through formation of the $[Cu(NH_3)_4]^{2+}$ complex. While chromium (III) hydroxide will also form $[Cr(NH_3)_6]^{3+}$, etc., ammonia solutions are much less basic than the sodium hydroxide used here. Thus they would not be expected to have the same effect on chromium (III) arsenate, consistent with minimal extraction of either chromium or arsenic by ammonia.

While no effective separation of chromium has been identified, it is possible to remove the arsenate content from sludge in a simple, inexpensive process using a small excess of strong base. The resulting solution can be used as a raw material for CCA manufacture. While some of the organic material does accompany the arsenate, this does not appear to have any detrimental effect on the product.

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5 Chemical oxidation

Reagents

It is highly desirable to recover the chromium (III) component of sludge by oxidising to chromium (VI). Any chemical oxidising agent must be strong, cheap, and only leave species already present in CCA. Only four reagents fit these stringent requirements:

Table 5.1 Reagents for chemical oxidation

Reagent	$E^{\ominus}_{red}$ vs. SHE (V)	Product
Nitrous oxide	1.77	Nitrogen
Hydrogen peroxide	1.78	Water
Ozone	2.08	Oxygen
Persulfate salts	2.12	Sulfate salts

Hydrogen peroxide would be convenient for CCA manufacturers, since it is also used in their arsenic acid production. Unfortunately peroxide also reduces the higher oxidation states of chromium, so the net result is catalytic decomposition of the peroxide by the chromium (III), with no chromium (VI) product.

Nitrous oxide N_2O is not redox active unless heated to at least 300 °C, so it is no use for solution chemistry. If a stream of hot N_2O was passed through a bed of dry sludge, it is possible that

$$3N_2O + 2CrAsO_4 \longrightarrow 3N_2 + 2CrO_3 + As_2O_5$$

but, above 250 °C;

$$4CrO_3 \longrightarrow 2Cr_2O_3 + 3O_2$$

so, while nitrous oxide might be able to dissociate chrome arsenate complexes into a mix of chromium and arsenic oxides, it could not achieve oxidation.

Dahlgren and Hartford[1] claimed that "ozone... can be used for reconstitution of CCA working solutions with a substantial content of trivalent chrome", though they gave no evidence. Sources within FTP disagreed. Still, ozone is one of the most powerful oxidising agents, and probably the cheapest since it is generated electrically. The equipment is inexpensive and readily available in a variety of sizes. However, the toxicity of this highly reactive gas could be a problem in practice. Considering the economic advantages, a preliminary experiment was carried out.

A bench scale ozone generator and pressure-swing oxygen generator were borrowed from Novozone (N.Z.) Ltd., Auckland. This equipment should have yielded about $3g.hr^{-1}$ ozone in 90% oxygen. The gas stream was run into the bottom of a dilute sludge solution, $[Cr^{III}] < 0.5\ gL^{-1}$, through Teflon tubing and a fish-tank bubbler. The solution became faintly bluer, but even after several hours no chromium (VI) could be observed. It was suggested that the degree of mixing was the problem, but fast mechanical stirring did not appear to help. Perhaps the gas stream needs to be passed over a spray or thin film of solution. Since so much ozone had failed to produce any reaction, no further experiments were conducted.

Fortunately, persulfate salts can achieve the desired result,

5.1 $$2Cr^{3+} + 3S_2O_8^{2-} + 8H_2O \longrightarrow 2HCrO_4^- + 6HSO_4^- + 8H^+$$

The common name 'persulfate' usually refers to peroxydisulfate, $S_2O_8^{2-}$, but may include peroxymonosulfate, HSO_5^-, which is unstable and therefore more expensive. The distinction will be emphasised here whenever it is particularly important. Despite their very high reduction potential, sodium and potassium peroxydisulfate are surprisingly stable and easy to handle. Since FTP formulations generally use sodium salts, sodium persulfate has been used for all the following trials.

Unlike the other oxidants, persulfates leave sulfate byproducts in solution. But oxide formulations of CCA contain no sulfate or other spectator ions. So persulfate only fits the selection criteria if CCA salt, or a solution which could be used in its manufacture, is an acceptable product.

Though it is an extremely strong oxidising agent, the peroxydisulfate ion $S_2O_8^{2-}$ is kinetically inert. Chromium (III) is also notoriously inert in aqueous solution. A reaction between the two is likely to need heating or catalysis. On the other hand, persulfate thermally decomposes to hydrogen peroxide, which would be counterproductive since it reduces chromium (VI). It is necessary to understand the kinetics of the system in order to find a balance between haste and waste.

Oxidation Kinetics

Persulfate kinetics are highly complex, vulnerable to the influence of the medium and of trace impurities (cf. the literature reviews by House[2], and Marsh and Edwards[3]). Since the literature values used in this chapter were obtained from a variety of sources, each using different substrates, different media, and different methods of chemical and statistical analysis, they may introduce some inaccuracies. Extrapolations from the results presented here should be treated with the usual caution.

Direct interaction between peroxydisulfate and reductant is difficult because the active peroxy region is so kinetically hindered. Thus the rate-determining step in persulfate oxidations is normally unimolecular decomposition into reactive radicals (cf. House[2]);

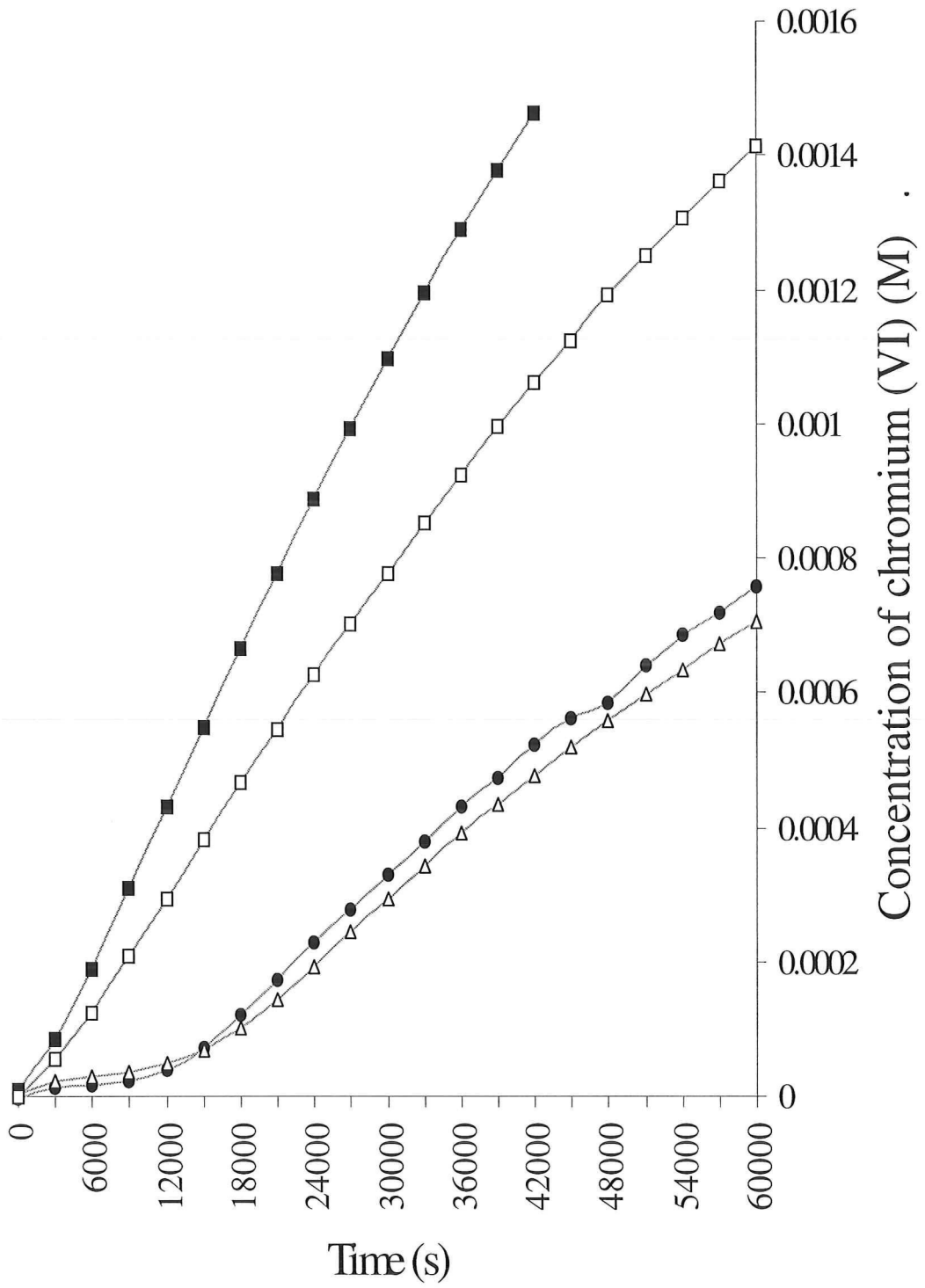
5.2 $S_2O_8^{2-} \longrightarrow 2SO_4^{\bullet-} \quad k = \left(1.1 \times 10^{17}\right) e^{-143000/RT} \ (s^{-1})$

The kinetic parameters are from the data of Kolthoff and Miller[4]. Frenneson and Fronaeus[5] observed that the chromium (III) oxidation rate was indeed dependent principally on persulfate concentration, and of the right order of magnitude. The results obtained here for various reactant concentrations are shown in Fig. 5.1. The rates are approximately twice as high as those of Frenneson and Fronaeus, probably because the medium is rather different. Their reactions are performed in at least 1 M perchlorate, whereas the ionic strength here is much lower.

A 0.0204 M solution of chromium (III) was prepared by adding 100 mL 2.5% hydrogen peroxide dropwise to 2.0484 g chromium (VI) oxide and 5.6 mL 99% sulfuric acid, diluted with several hundred mL water. The solution was boiled for 8 hr to remove excess H_2O_2 and made up to 1L. After this time, a 10 mL aliquot produced no visible iodine colour when shaken with ca. 0.1 g KI and ca. 2 mL chloroform. The solution had a pH of 1.8. In each reaction, 25 mL substrate was diluted to 250 mL, then one equivalent of sodium persulfate, 0.1825 g, was added. Unless further modified with sulfuric acid or sodium hydroxide, the pH was then 2.2.

Reactions were carried out in a stoppered quartz cell, pathlength 1.00 cm, placed in the beamline of a Hewlett-Packard HP8452A diode array ultraviolet-visible spectrophotometer. Approximately 3 mL of stirred cool solution was pipetted into the cell, which had been pre-heated to the reaction temperature of 60 °C using a cell block and controller built in the Department. This heating apparatus appeared to be accurate to within half a degree, and to drift over no more than half a degree during a twenty-hour run. Spectra were taken every 300 seconds. Raw absorbances at 350 nm were converted to chromium (VI) concentrations using an extinction coefficient of 72500 M^{-1}, obtained from a 1.05 mM sodium dichromate standard. The absorbances did not drift significantly during runs, nor were they affected by ambient lighting.

Figure 5.1 Effect of varying reagent concentrations



● Standard reaction: 0.00204 M Cr^{3+}, 1 equiv. $S_2O_8^{2-}$, 333.2 K
❑ 1.5 equivalents $S_2O_8^{2-}$
■ 2 equivalents $S_2O_8^{2-}$
Δ 2 equivalents Cr^{3+}

Frenneson and Fronaeus prefer the decomposition step

$$S_2O_8^{2-} + H_2O \longrightarrow SO_4^{\bullet-} + OH^{\bullet} + HSO_4^-$$

although the mechanism of this step is not obvious. Sulfate and hydroxyl radicals are interconvertible[3]*:*

$$SO_4^{\bullet-} + H_2O \longrightarrow OH^{\bullet} + HSO_4^- \qquad k^{\varnothing} < 3 \times 10^{-3} s^{-1}$$

$$OH^{\bullet} + SO_4^{2-} \longrightarrow SO_4^{\bullet-} + OH^- \qquad \text{no data available}$$

$$SO_4^{\bullet-} + OH^- \longrightarrow OH^{\bullet} + SO_4^{2-} \qquad k^{\varnothing} = 8 \times 10^7 M^{-1} s^{-1}$$

Since two anions are extremely unlikely to react together, the rate constant given for the latter process seems implausible. Then the equilibrium ought to favour the less active sulfate radicals (cf. Prakash et al.[6]*).*

Frenneson and Fronaeus also observed a slight chromium dependence. Roughly, their rate halved when the ratio $[Cr^{3+}]_0:[S_2O_8^{2-}]_0$ *increased by an order of magnitude. This was attributed to increased formation of stable chromium (III) peroxydisulfate complexes. But it was observed here that the UV spectrum for the hexaquochromium (III) sulfate complex does not change when persulfate is added. Therefore any new complexes must also be outer-sphere. It seems unlikely that the persulfate would be stabilized much by that arrangement. Further, in the cases where* $[Cr^{3+}]:[S_2O_8^{2-}]$ *changes substantially during their reaction, there is no indication of any corresponding change in the rate.* $[Cr^{3+}]_0$ *did not vary as much here, so it is difficult to confirm or explain their observations.*

Using the rate law for a first order decomposition; let $[S_2O_8^{2-}] = S$; $S = S_0$ when $t = 0$,

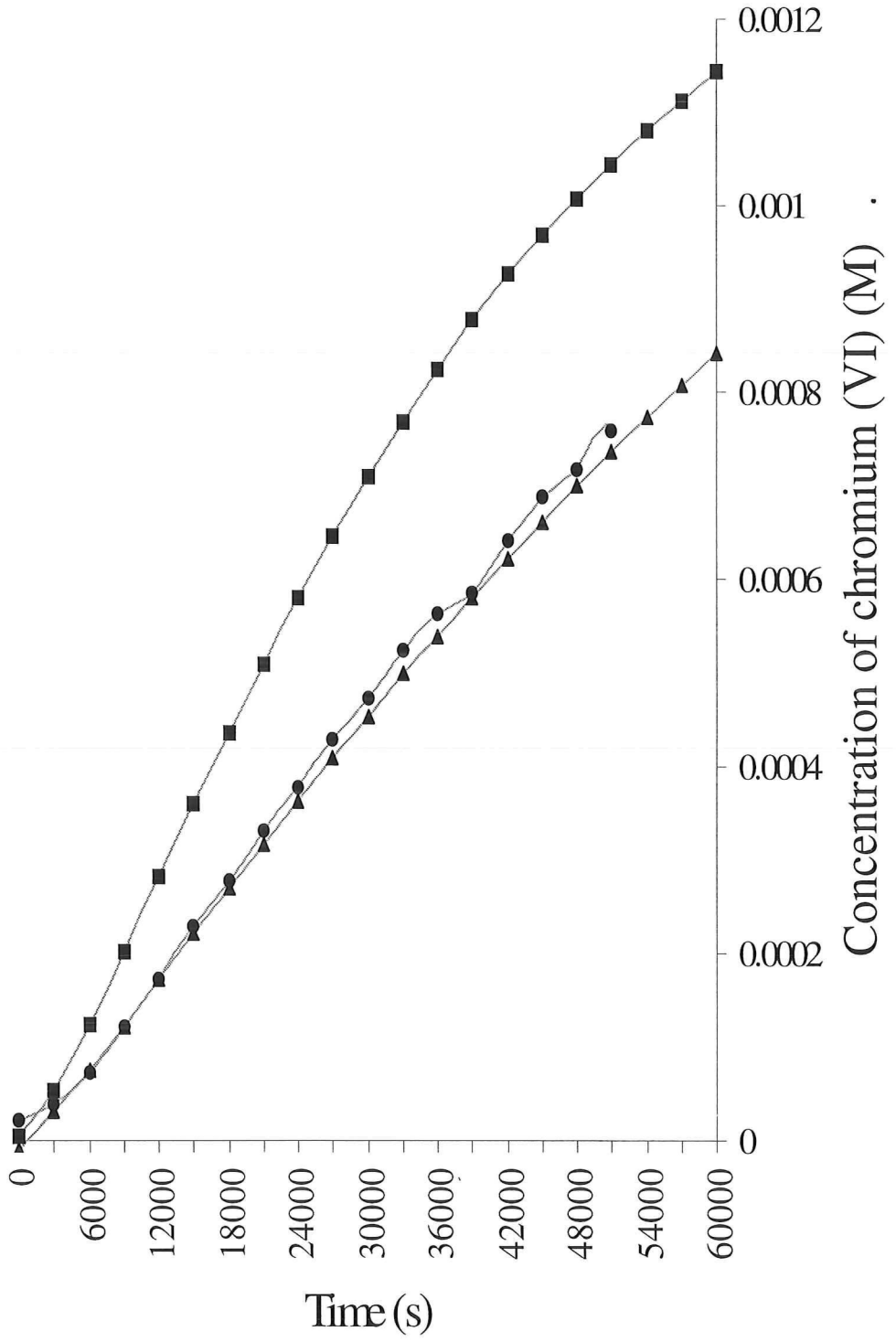
$$\frac{dS}{dT} = -k_1 S$$

and integrate to obtain

5.3 $$S = S_0 e^{-kt}$$

Fig. 5.1 shows that this expression is inadequate. The decay curves are not exponential, even allowing for an induction period. The order with respect to peroxydisulfate appears slightly greater than unity.

Figure 5.2 Effect of varying acidity



● Standard reaction: initial pH 2.2
▲ Initial pH adjusted to 3
■ Initial pH adjusted to 1.0

Fig. 5.2 shows some hydrogen ion dependence. It is known that peroxydisulfate can undergo an acid-catalysed decomposition to peroxymonosulfate[2];

5.4 $$S_2O_8^{2-} + H_2O \xrightarrow{H^+} HSO_5^- + HSO_4^- \quad k = \left(6.3 \times 10^{13}\right) e^{-111000/RT} \left(s^{-1}\right)$$

Again, the kinetic parameters are from Kolthoff and Miller. Chromium (III) oxidation must be carried out in acid conditions to avoid precipitating chromic arsenates, hydroxides, etc.. The oxidation liberates at least eight hydrogen ions for every three persulfate consumed [Eqn. 5.1] so it is partly autocatalytic.

Peroxymonosulfate is also a very strong oxidant which ought to oxidise chromium (III), although it too can decompose (cf. Ball and Edwards[7]). If it is an effective oxidant, the rate of oxidation should increase in sufficiently acidic conditions. If it is ineffective, the rate should decrease even though the unimolecular rate constant is unchanged.

Frenneson and Fronaeus failed to take this effect into account in their analysis. Thus their mechanism

Cr^{3+} + *radical* $\longrightarrow$ Cr^{IV} + *ion* *followed by either*

$Cr^{IV} + 2SO_4^{\bullet-} \longrightarrow \longrightarrow Cr^{VI} + 2SO_4^{2-}$ *or, at sufficient acidity,*

$Cr^{IV} + H_2SO_5 \longrightarrow Cr^{VI} + SO_4^{2-} + H_2O$

should lead to declining rates with decreasing pH, not identical rates below pH 1 as they propose.

This mechanism led Frenneson and Fronaeus to conclude that "two chromium (III) ions are oxidised to chromium (VI) for every peroxydisulfate ion disappearing in the uncatalysed decomposition". That is, the loss due to oxidation would be three times the rate of unimolecular decomposition. The data obtained here do not support that conclusion. Their paper does not give raw data, only graphs which are too small to read accurately, but it does not seem that their own data is consistent either.

Samal *et al.*[8] investigated chromium (III) catalysis of HSO_5^--initiated acrylonitrile polymerisation. They believe that catalysis arises from interaction between the chromic ion and the peroxy region of HSO_5^-. A complex forms and then decays into reactive intermediates; Cr^{IV}, and $OH^{\bullet}$ or $SO_4^{\bullet-}$. That is direct oxidation, plus the generation of an oxidising radical. So it is probable that peroxymonosulfate is an effective oxidant. Similar processes occur for other transition metal ions such as cobalt (II), cerium (IV), and manganese (II), although each of those systems has rather different kinetics[3].

Samal *et al.* were unable to account quantitatively for the interaction between peroxymonosulfate and chromic ion. They proposed a complicated reaction scheme, with the termination step varying according to conditions. They deduced that, at low temperatures and catalyst concentrations, the polymer radicals underwent mutual recombination. Above 35 °C or 0.02 M Cr^{III}, they were predominantly quenched by higher valency chromium species. So the kinetics would probably have been quite different without acrylonitrile. Still, the catalysed peroxymonosulfate reaction appeared to be much faster than peroxydisulfate decomposition at the same temperature.

Assuming peroxymonosulfate oxidises chromium (III) quickly and efficiently, and allowing for autocatalysis, the rate law is considerably more complicated;

$$\mathbf{5.5} \qquad \frac{dS}{dt} = -k_1 S - k_2 S\left(\left[H^+\right]_0 + \frac{8}{3}\left(S_0 - S\right)\right)$$

Let $H_0 = [H^+]_0$, $A = k_1 + k_2 H_0 + {}^8/_3 k_2 S_0$, $B = {}^8/_3 k_2$,

$$\int \frac{dS}{AS - BS^2} = \int -dt$$

$$\frac{1}{A} \ln\left|\frac{-2BS}{-2BS + 2A}\right| = -t + C$$

$$\frac{BS}{A - BS} = C^* e^{-At}$$

The unknown can be removed by considering t = 0;

$$C^* = \frac{BS_0}{A - BS_0}$$

$$e^{-At} = \left|\frac{S\left(BS_0 - A\right)}{S_0\left(BS - A\right)}\right|$$

$$\mathbf{5.6} \qquad S = \frac{AS_0 e^{-At}}{A + BS_0\left(e^{-At} - 1\right)}$$

There are a few special cases:

$A \gg BS_0$ $\quad (k_1 \gg {}^8/_3 k_2 S_0$ *and/or* $H_0 \gg {}^8/_3 S_0)$ $\quad S = S_0 e^{-k_1 t - k_2 H_0 t}$

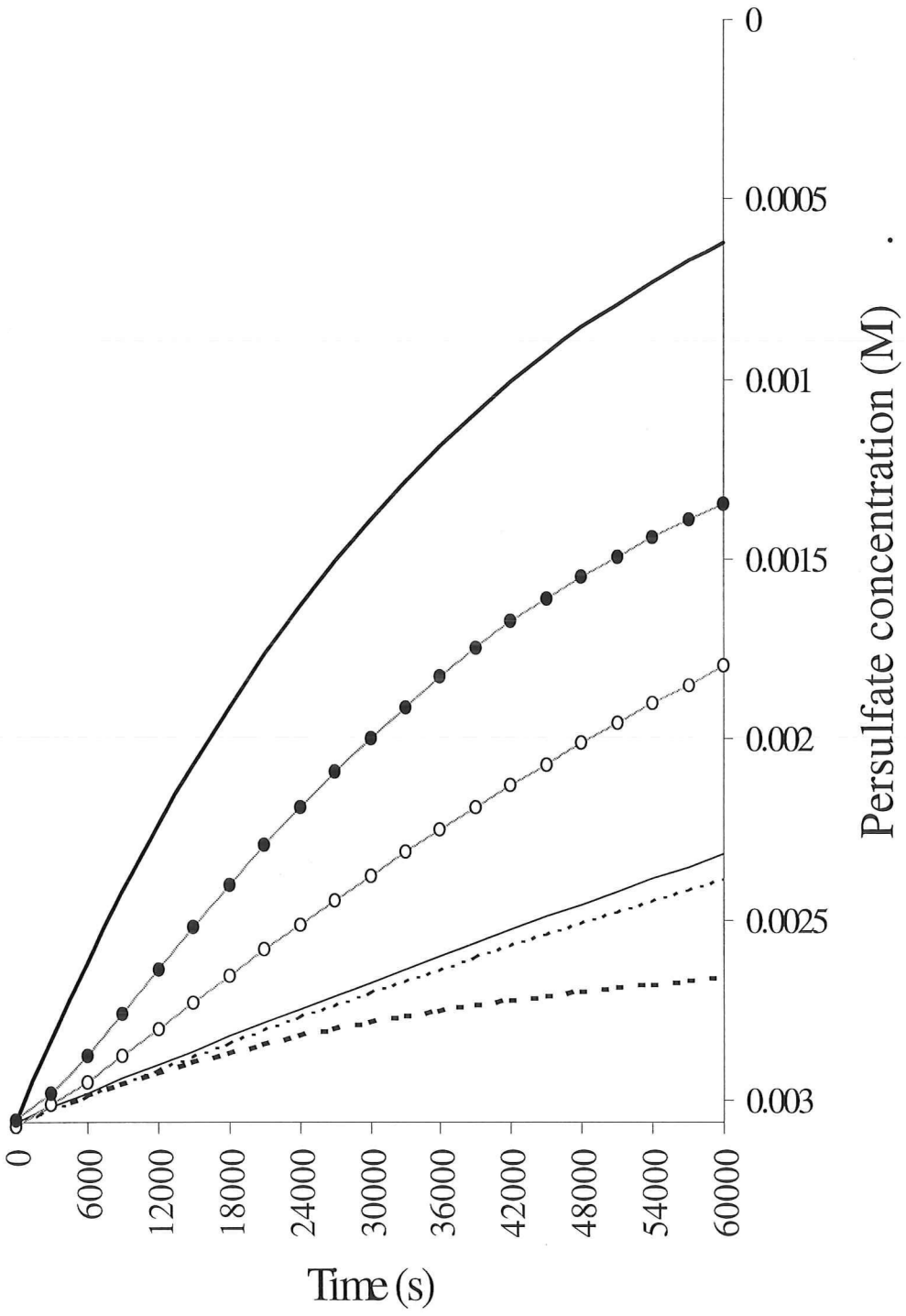
$A = BS_0$ $\quad (k_1 \ll {}^8/_3 k_2 S_0$ *and* $H_0 \ll {}^8/_3 S_0)$ $\quad S = S_0$

In the first case, there is no autocatalysis, either because the acid-catalysed rate constant is relatively small, or because the initial acidity is relatively high. In the second case there is no decomposition because the unimolecular rate constant and the initial acidity are negligible.

It is non-trivial to extract the unimolecular component U analytically, but simple enough to obtain it numerically, by substituting $[S_2O_8^{2-}]$ from Eqn 5.6 into Eqn 5.3 over reasonably short intervals.

5.7 $\quad U_{t+\Delta t} \approx U_t - S_t\left(1 - e^{-k_2 \Delta t}\right)$

Figure 5.3 Persulfate decomposition at pH 1.0 and pH 3



$[S_2O_8^{2-}]$ = 0.00306 M, T = 333.2 K

	pH 1.0	pH 3
Observed loss through Cr^{III} oxidation	●	○
Predicted total decomposition	———	———
Predicted unimolecular decomposition	·····	·····

Fig. 5.3 shows that Eqns. 5.6 or 5.7 are insufficient to explain the observations. Additional steps such as

$$Cr^{IV} + H_2SO_5 \longrightarrow Cr^{VI} + H^+ + HSO_4^- \quad \text{and}$$
$$Cr^{IV} + S_2O_8^{2-} \longrightarrow Cr^{VI} + 2SO_4^{2-}$$

would allow one radical to generate more than $^1/_3$ Cr^{VI}, accelerating the reaction. Conversely, oxidant could be wasted in forming byproducts[2,3,9]. For example, Frenneson and Fronaeus observed that oxygen evolution increased rapidly with increasing acidity. This cannot result from direct bimolecular termination

$$2HSO_5^- \longrightarrow O_2 + 2HSO_4^-$$

since two anions will not readily react together. So the oxygen must be produced by radical chemistry, probably including the elementary propagation steps

$$H_2SO_5 + OH^\bullet \longrightarrow HSO_5^\bullet + H_2O \quad k^\varnothing = 3\times10^8\ M^{-1}s^{-1}$$
$$H_2SO_5 + HSO_4^\bullet \longrightarrow HSO_5^\bullet + H^+ + HSO_4^- \quad k^\varnothing < 10^5\ M^{-1}s^{-1}$$

and termination steps

5.8 $2HSO_5^\bullet \longrightarrow O_2 + 2SO_4^{\bullet-} + 2H^+ \quad k^\varnothing = 2\times10^6\ M^{-1}s^{-1}$

5.9 $2OH^\bullet \longrightarrow H_2O_2 \quad k^\varnothing = 1\times10^{10}\ M^{-1}s^{-1}$

$2HSO_4^\bullet \longrightarrow S_2O_8^{2-} + 2H^+ \quad k^\varnothing = 4\times10^8\ M^{-1}s^{-1}$

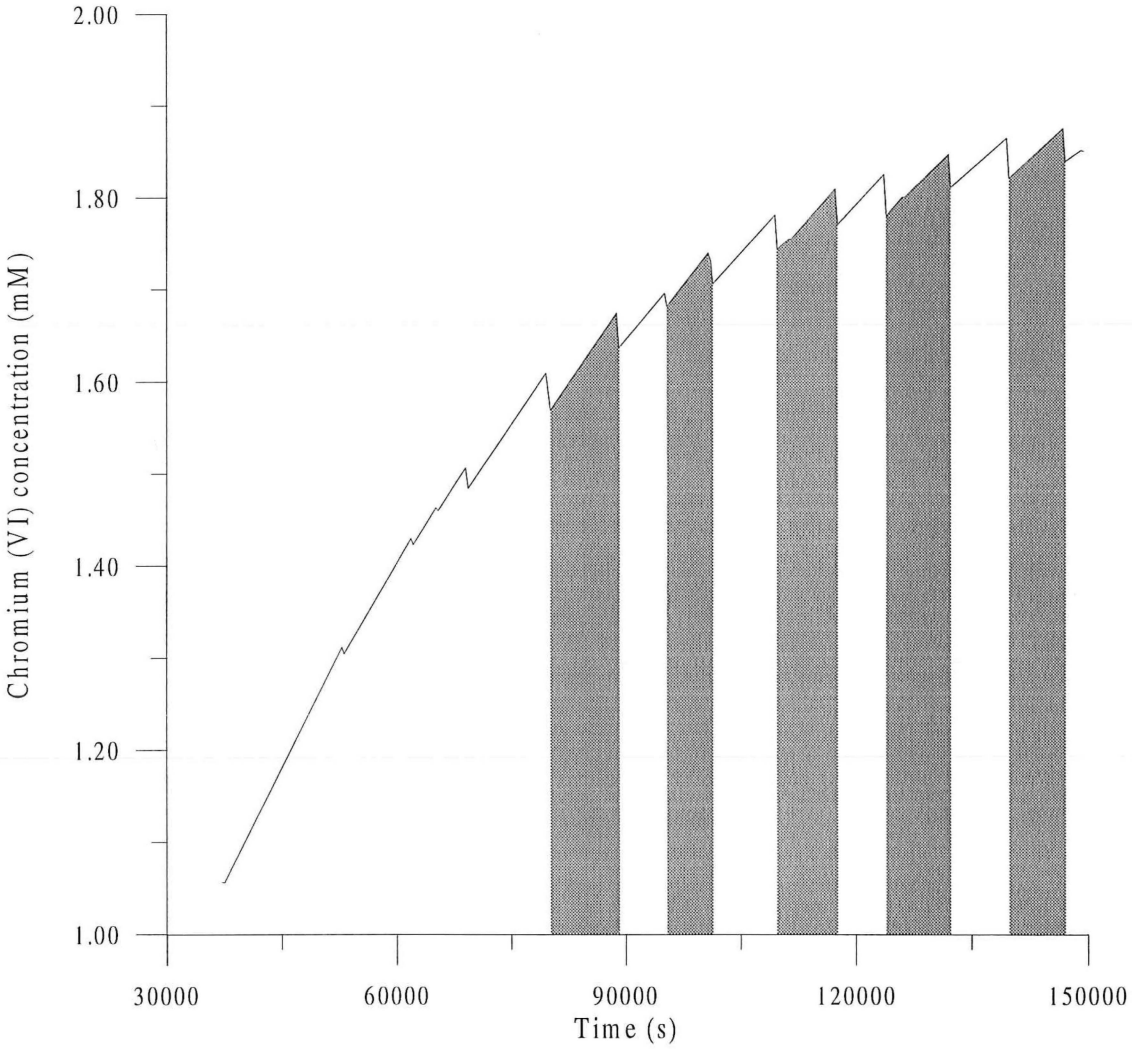
and possibly $HSO_4^\bullet + OH^\bullet \longrightarrow H_2SO_5$ not known

with rate constants from Marsh and Edwards. When the termination reactions Eqns. 5.8 and 5.9 become competitive with oxidation, persulfate is wasted. The oxygen-generating reaction Eqn. 5.8 requires peroxymonosulfate, produced by acid-catalysed decomposition [Eqn. 5.4]. Therefore excess acidity should decrease reaction efficiency. All the radical recombinations are bimolecular, therefore they become rapidly more effective as radical concentrations rise. It follows that excess heat or persulfate will also decrease efficiency.

A steady-state analysis appears inappropriate since none of the radicals, nor the peroxymonosulfate, will be in steady states. $HSO_5^\bullet$ will not even appear until later in the reaction, which is typical of peroxymonosulfate reactions[3]. A numerical solution might be possible, except that the rates of the reactions between the various radicals and chromium (III) are not known. Currently, then, Eqn. 5.8 cannot be improved to account for either oxygen or peroxide evolution.

Fig. 5.4 reflects the complexity of the situation. During the pH 1.0 oxidation, the absorbance at 350 nm did not increase monotonically. Instead it began to oscillate sharply every 2 - $2^{1}/_{2}$ hours, as if some of the chromium (VI) had suddenly been reduced by peroxide. This behaviour was not seen in pure chromium (VI) solutions monitored under the same conditions. Other kinetic runs exhibited similar phenomena.

Figure 5.4 Oscillating reduction late in the reaction

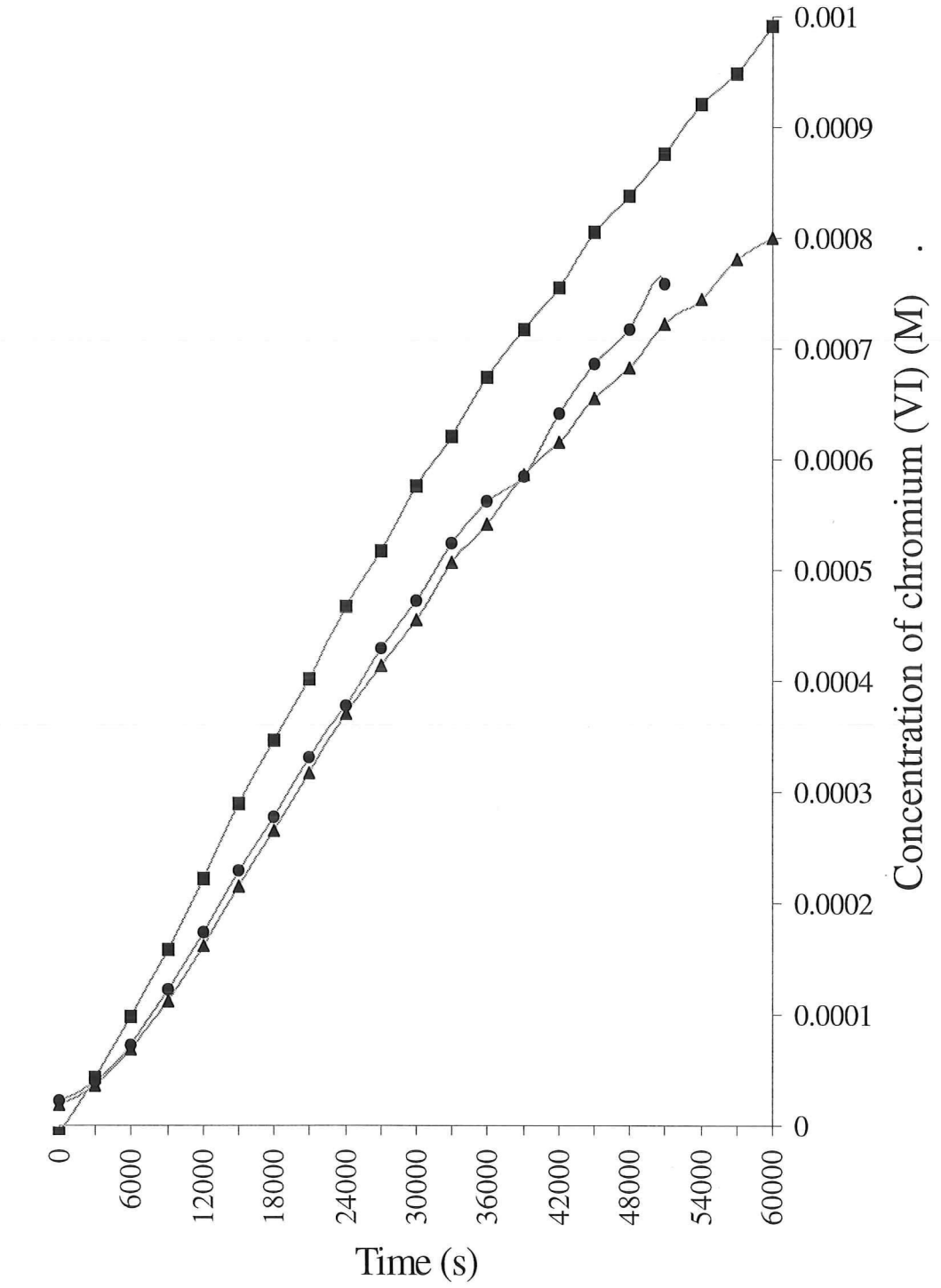


Only points immediately before and after each dip have been plotted. The curve rises monotonically and fairly smoothly between dips, and up until 30000 seconds.

Under these conditions, arsenate has little or no effect on the reaction, whether added to hexaquochromium (III) or introduced in sludge solution, as chromium arsenato oligomers [Fig. 5.5]. However, there was still concern that the oligomers might have dissociated to an unrealistic degree in such dilute solution, masking any possible inhibition at concentration. Therefore, sludge was dissolved in 5 equivalents of boiling arsenic acid [cf. Ch. 3], cooled, filtered, and diluted to give an emerald green solution, 0.109 M '$H_{2.5}AsO_4^{-0.5}$'. This solution was brought to the boil and one equivalent of sodium persulfate was added over a five minute period. Even though the solution must have been strongly buffered to an apparently favourable pH = $pK_a(H_3AsO_4)$ = 2.25, there was absolutely no visible reaction. It follows that persulfate treatment will not work on sludge solutions or work solutions until the oligomers have been dissociated. Presumably any other strongly coordinating anion will have a similar effect.

Persulfate could potentially be removed by reaction with impurities in the solution, too. The most likely source would be the ca. 5% organic content of sludge [Ch. 2]. However, acid-catalysed polymerisation and filtering has already removed the majority of this material [Ch. 3].

Figure 5.5 Effect of adding arsenate



● Standard reaction
▲ With 1 equivalent $HAsO_4^{2-}$
■ Sludge solution with the same $[Cr^{III}]$

Silver (I) can apparently catalyse any persulfate reaction via the silver (II) and (III) states[2,3]. Because the silver interacts directly with the persulfate to form a potent and unhindered oxidiser, the activation energy for the catalysed pathway is inevitably much lower. Rates improve dramatically.

Thompson[9] reported an interesting dual catalysis in strong acid;

$$2HSO_5^- \xrightarrow{Ag^+, S_2O_8^{2-}} O_2 + 2H^+ + 2SO_4^{2-}$$

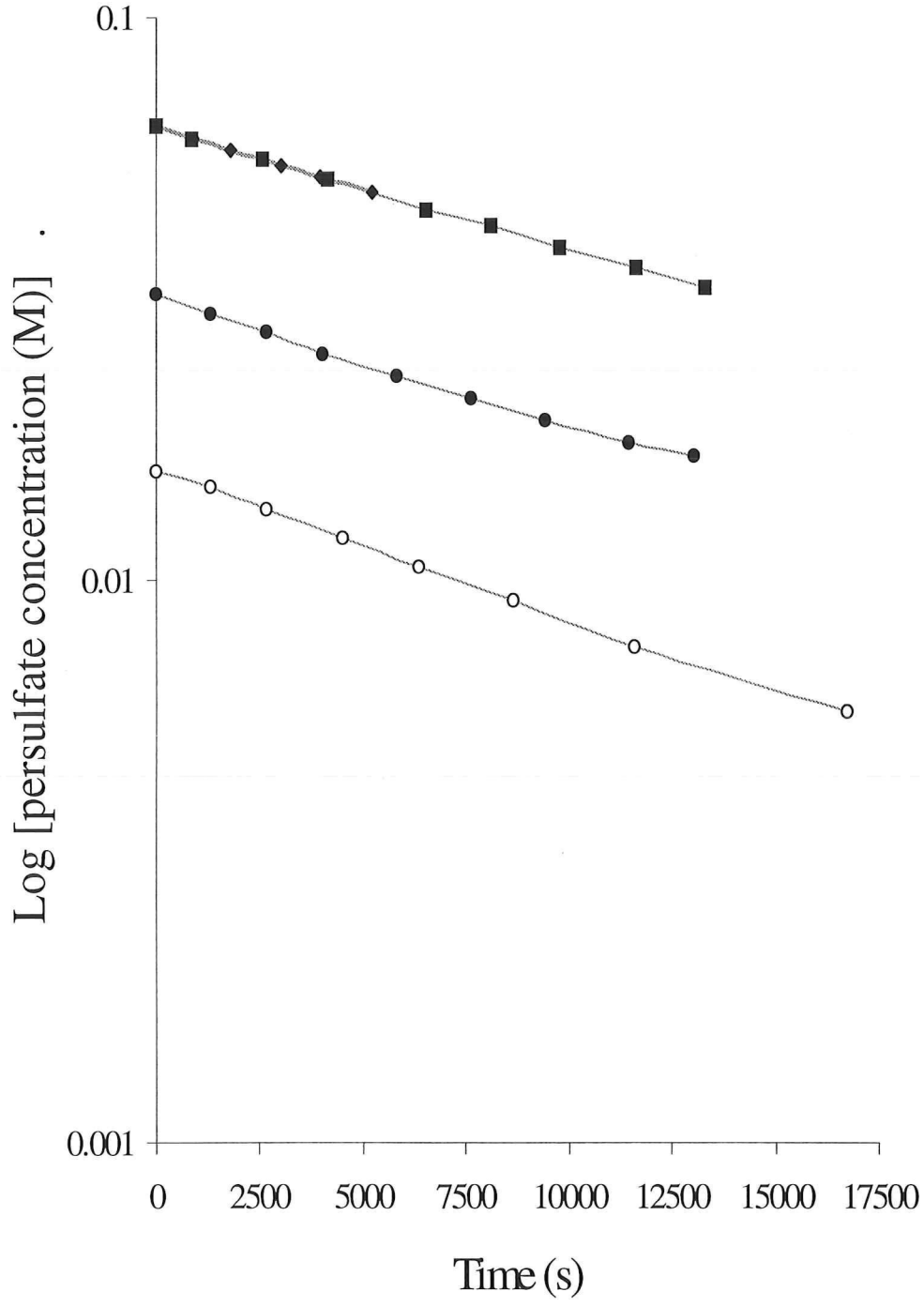
where the $S_2O_8^{2-}$ is first consumed in producing high-valent silver, and then regenerated by radical recombination. From Thompson's data, the Arrhenius parameters can be estimated very roughly as A = 6 x 10^9 $M^{-1}s^{-1}$, E_a = 62 $kJmol^{-1}$ (cf. Prakash *et al.*[6]). This pathway appears to cause most of the decomposition under his reaction conditions; typically 17 °C, 0.5 M $HClO_4$, 0.016 M HSO_5^-, 0.006 M $S_2O_8^{2-}$, 0.008 M Ag^+. The decomposition can also be catalysed by Co^{2+} alone, although the mechanism is more complicated still.

Yost[10] investigated the silver-catalysed oxidation of chromium (III) as early as 1926. Room-temperature reactions were quenched with HCl, then [Cr^{VI}] was determined titrimetrically using $VOSO_4$. From the initial rates of reaction he deduced that

$$\frac{d}{dt}\left[S_2O_8^{2-}\right] = k_2\left[S_2O_8^{2-}\right]\left[Ag^+\right]$$

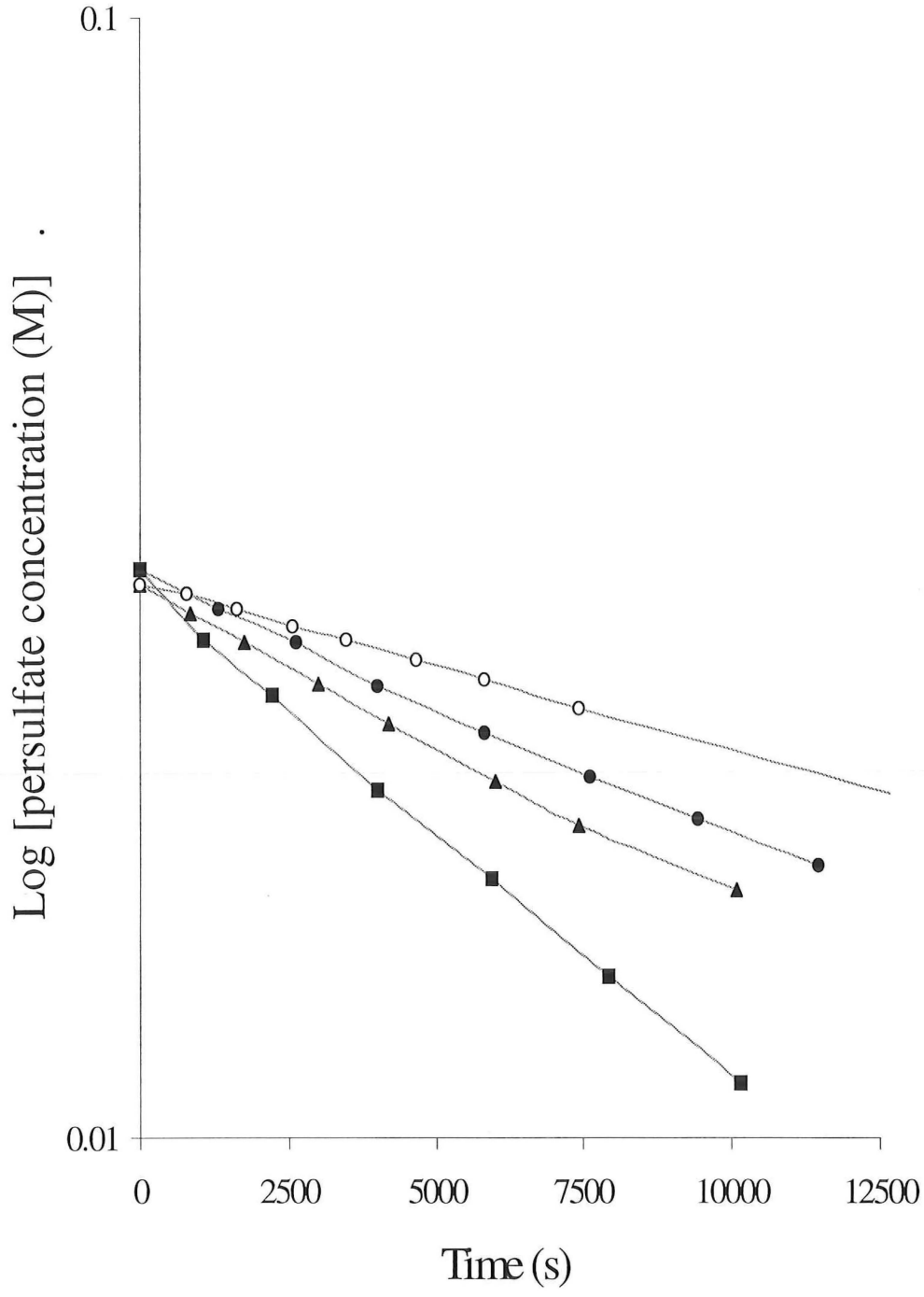
A close examination of his data suggests that this may be a little simplistic. The numbers from his experiments 1, 2, 3, 5, 9, 10, and 11 have been plotted on the following pages, using a log scale for concentration. Since the lines in Fig. 5.6 are straight, parallel and equally spaced, it is reasonable to deduce that the reaction kinetics are indeed first order in persulfate and independent of chromium. But from Fig. 5.7 it seems that $[H^+]_0$ also has some effect on the rate. Because Yost never followed the reaction past 8% conversion, there is no point in suggesting any alternative rate equation from his results.

Figure 5.6 Effect of changing reactant concentrations [10]



● Yost's experiment 3: 0.0218 M Cr^{3+}, 1 equiv. $S_2O_8^{2-}$, 298 K
■ experiment 1: as #3 but 2 equivalents $S_2O_8^{2-}$
◆ experiment 2: as #3 but 2 equivalents $S_2O_8^{2-}$, 0.01 M Cr^{3+}
○ experiment 11: as #3 but $^1/_2$ equivalent $S_2O_8^{2-}$, 0.01 M Cr^{3+}

Figure 5.7 Effect of changing catalyst concentrations [10]



● Yost's experiment 3: 0.0218 M Cr^{3+}, 0.01 M Ag^{+}, 0.2 M H^{+}
■ Experiment 5: as #3 but 0.02 M Ag^{+}
▲ Experiment 9: as #3 but 0.1 M H^{+}
○ Experiment 10: 0.01 M Cr^{3+}, 0.01 M Ag^{+}, 0.1 M H^{+}

A study by Prakash *et al.*[6] agreed broadly with Yost. Again, only the initial rate was considered; again, the kinetics were chromium independent and apparently first order in silver ion and persulfate. They also observed hydrogen ion catalysis, and rate retardation by bisulfate ion and acrylamide. For mechanistic reasons they suggested that

$$\frac{d}{dt}\left[Cr^{VI}\right] = \frac{2k_1K_1\left[Ag^{I}\right]\left[S_2O_8^{2-}\right]}{1+K_1\left[S_2O_8^{2-}\right]+K_2\left[HSO_4^{-}\right]}$$

with constants

$$k_1: \quad AgS_2O_8^- + H_2O \longrightarrow Ag^{2+} + OH^\bullet + HSO_4^- + SO_4^{2-}$$

$$K_1: \quad Ag^+ + S_2O_8^{2-} \longleftrightarrow AgS_2O_8^-$$

$$K_2: \quad Ag^+ + HSO_4^- \longleftrightarrow AgHSO_4$$

That is, silver ions already complexed by peroxydisulfate or bisulfate are not available to catalyse the reaction. It would be simpler to write

$$\frac{d}{dt}\left[Cr^{VI}\right] = 2k\left[Ag^{+}\right]\left[S_2O_8^{2-}\right]$$

They then suggest that the retarding effect of bisulfate ion could equally well be ascribed to

$$HSO_4^- + OH^\bullet \longrightarrow SO_4^{\bullet-} + H_2O$$

since $SO_4^{\bullet-}$ is less active; or even to

$$Cr^{3+} + SO_4^{2-} \longrightarrow CrSO_4^+$$

assuming that this complex is less active than the free ion. These explanations are less convincing. The rate-determining step is the reaction of silver with persulfate, not the interaction of the radicals and the chromium (III). The latter reason is particularly weak since their sulfate was already in vast excess of $[Cr^{3+}]$ before addition of bisulfate, the formation of an inner-sphere complex should have shown up in their UV spectra, and the kinetics ought then to be slightly chromium-dependent. Of course, the inhibitors may also slow the measured rate by removing radicals. This is certainly how acrylonitrile acts, but surely not bisulfate.

For the same reason, they are probably incorrect to ascribe hydrogen ion catalysis to the increased reactivity of $HSO_4^\bullet$ over $SO_4^{\bullet-}$. The increase in H^+ must affect the $AgS_2O_8^-$ intermediate, either by favouring its formation, or by hastening its decomposition. Again, only the initial rate was measured, so it is difficult to offer an alternative.

In any event, their overall rate constant for chromium (VI) formation was well described by

$$k = \left(1.8 \times 10^{8}\right) e^{-58500/RT} \quad \left(s^{-1}\right)$$

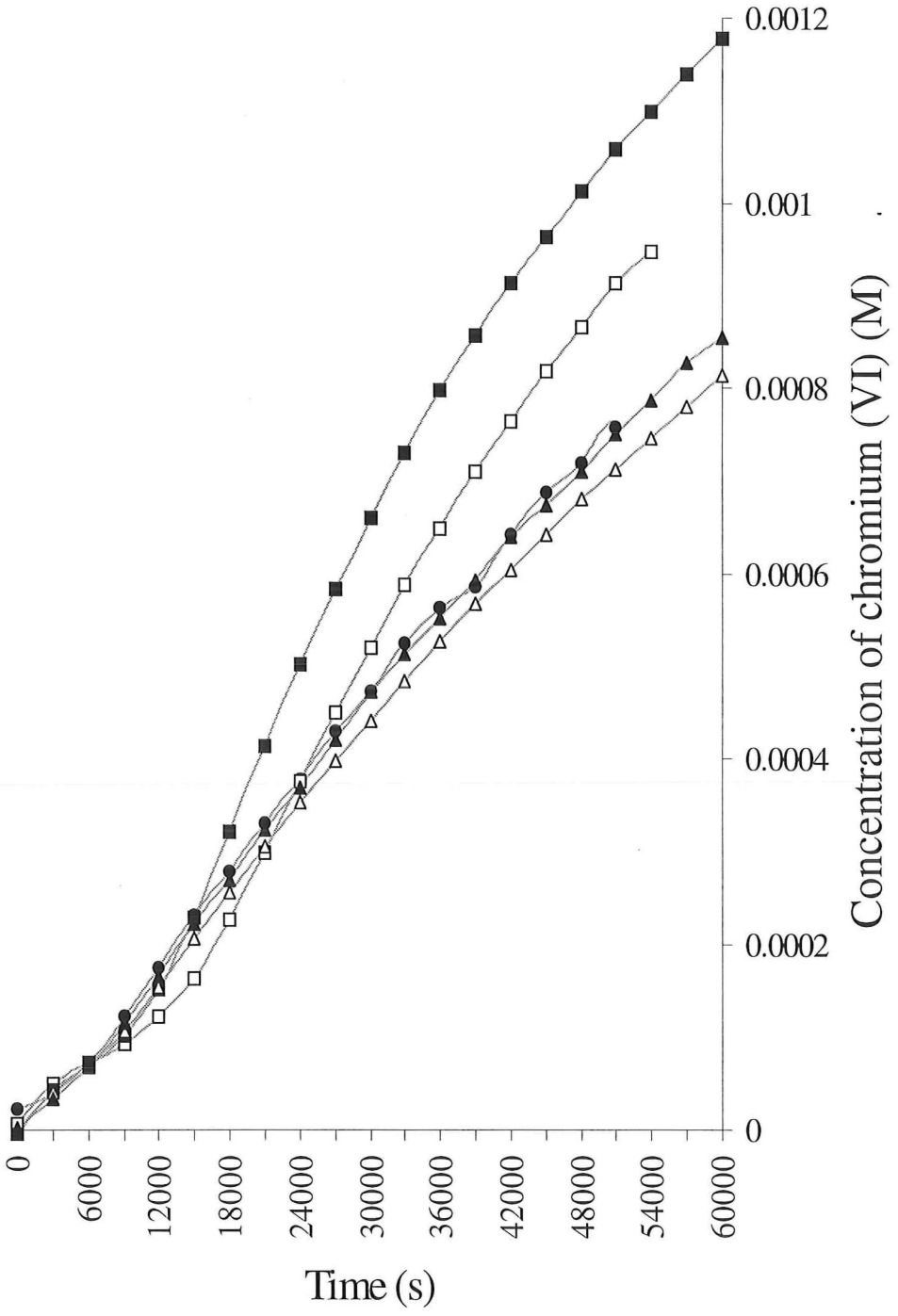
Similarly, copper (II) ion catalyses some peroxydisulfate reactions via conversion to unstable copper (III) intermediates, which are excellent oxidising agents[2]. It would be most convenient if it catalysed chromium (III) oxidation, because there is already quite a lot of copper in sludge.

Ball and Edwards[11] report strong catalysis of H_2SO_5 decomposition by Co^{II} and Mo^{VI}; weak catalysis by Ni^{II}, Cu^{II}, Ru^{II}, Ir^{III}, V^{V} and W^{VI}; and no effect for Ag^{I}, Tl^{I}, Zn^{II}, Cd^{II}, Pd^{II}, Hg^{II}, Pb^{II}, Fe^{III}, Sb^{III}, Ce^{III}, Bi^{III}, Rh^{IV}, Zr^{IV}, Pt^{IV}, Th^{IV}, Ta^{V}, I^{V}, Cr^{VI}, or Mn^{VII}. Since they found no effect for silver (I), these results may not be reliable.

In this study, copper (II) and silver (I) were added to the standard kinetic run [Fig. 5.8]. There is nothing surprising in the results; the perturbation with silver appears to be proportional to the amount added, and copper appears to have little effect.

An 8.36 mM solution of copper (II) was prepared from $CuSO_4{\cdot}5H_2O$, a 1.00 mM solution of silver (I) was prepared from Ag_2SO_4 in 0.1% H_2SO_4. The concentrations were chosen such that, when 10 mL catalyst was added to 25 mL substrate, $[Ag^{+}]$ was 2% of $[Cr^{3+}]$, and $[Cu^{2+}]$:$[Cr^{3+}]$ was the same as in sludge solution. Thereafter, the solutions were treated as in the previous experiments.

Figure 5.8 Effect of catalysis



● Standard reaction
❑ With 40 μM Ag^{I}
■ With 80 μM Ag^{I}
Δ With 0.33 mM Cu^{2+}
▲ With 0.66 mM Cu^{2+}

Prakash *et al.*[6] observed an induction period which was, roughly, inversely proportional to their initial persulfate concentration. Since the induction period here is an order of magnitude larger, and persulfate concentration is an order of magnitude lower, that rule seems quite applicable.

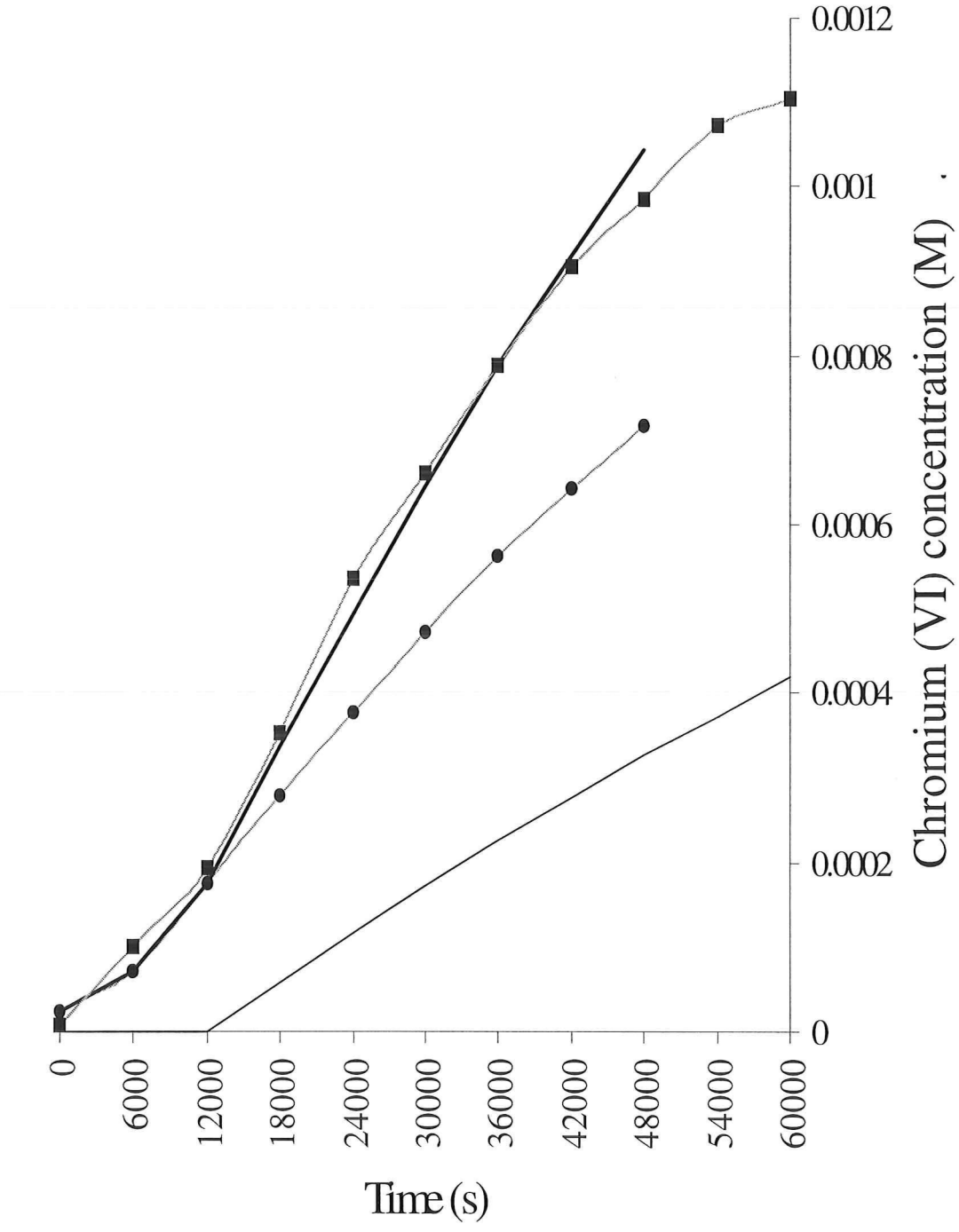
It is surprisingly difficult to calculate the expected increase in rate due to silver (I) catalysis. Let that increase be A, take $k_{333.7K} = 0.125\ M^{-1}s^{-1}$, assume that complex formation is minimal so that $[Ag^+] = [Ag^I] = 4 \times 10^{-5}M$, approximate $[S_2O_8^{2-}]$ with the data from the standard uncatalysed experiment S_{obs}, and allow for an induction period of about 12000 seconds;

$$\mathbf{5.10} \quad A_{t+\Delta t} = A_t + k\left[Ag^I\right]S_{obs}\Delta t \quad \forall t: t > 12000$$

Fig. 5.9 compares this expression with the observations. While the agreement is not bad, as the reaction progresses the calculated value drops away from the observed value. This could be expected because $[S_2O_8^{2-}]$ is actually less than S_{obs}, but formation or even precipitation of $AgCr_2O_7^-$ complexes may be partly responsible.

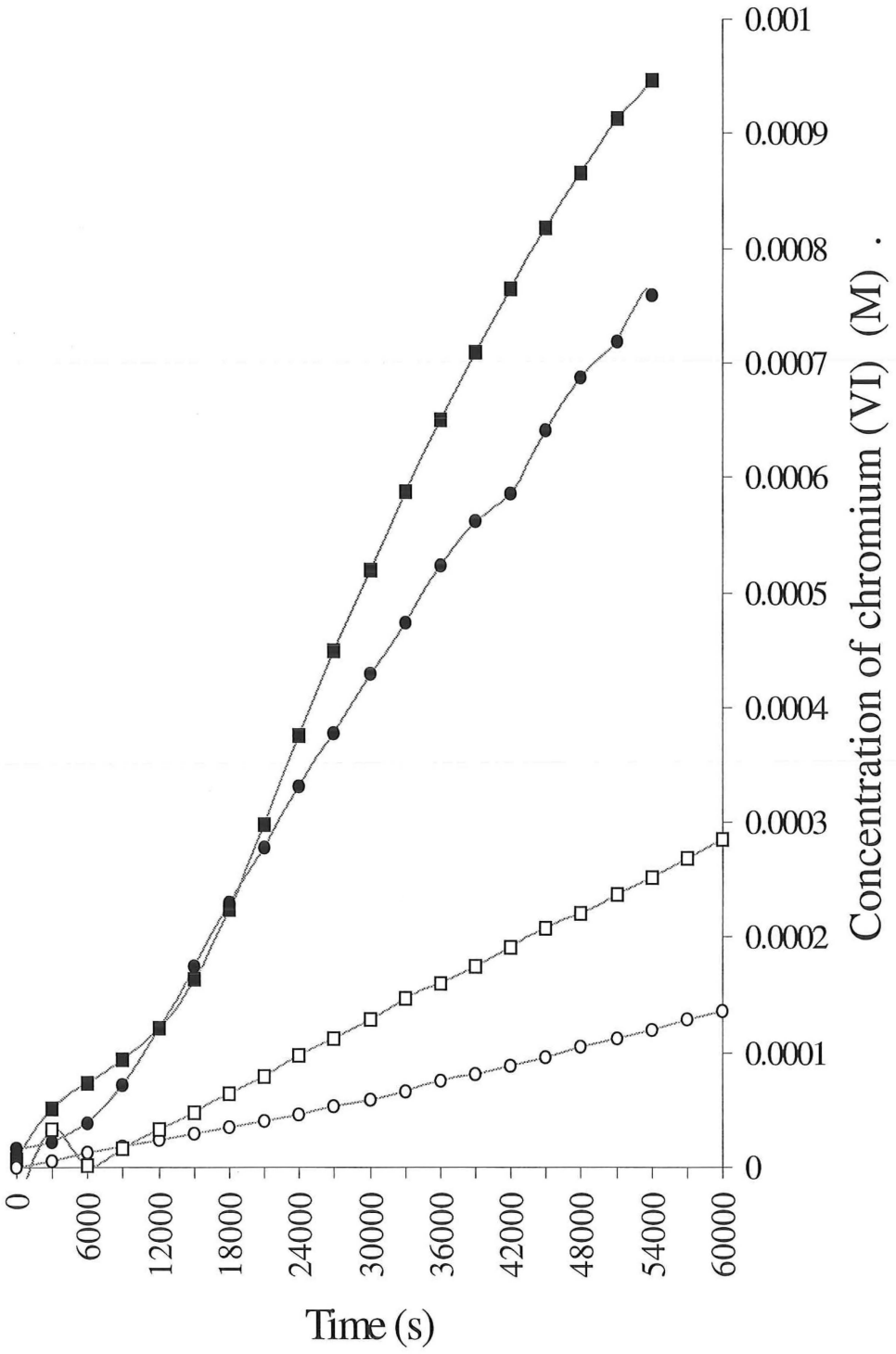
Figure 5.10 shows the effect of adding silver (I) sulfate at two temperatures, 45° and 60°. Assuming simple Arrhenius kinetics, the activation energies can be estimated very roughly as 115 $kJmol^{-1}$ uncatalysed, 75 $kJmol^{-1}$ Ag^I-catalysed. This may be stretching the data too far, for Prakash *et al.*[6] have only 60 $kJmol^{-1}$ for the catalysed oxidation. Further, the energies should be the same as those for decomposition, which is supposed to have the same rate-determining step. But while House's typical value of 75 $kJmol^{-1}$ for the catalysed reaction is in agreement[2], Kolthoff and Miller[4] have an uncatalysed E_a of 143 $kJmol^{-1}$. Probably the assumption is invalidated by the number of processes operating. It may take a considerable amount of work to determine the relationship between these rate constants and temperature.

Figure 5.9 Comparisons of model and observations of Ag^{I} catalysis



Standard reaction
With 40 μM Ag^{I}
Predicted additional Cr^{VI} due to 40 μM Ag^{I}
Sum of standard reaction and predicted increase

Figure 5.10 Effects of temperature and silver catalysis



● Standard reaction (333.2 K)
■ With 40 μM Ag^I
○ At 318 K
❑ With 40 μM Ag^I at 318 K

Tsao and Wilmarth[12] were the first to report on photolysis of persulfate by ultraviolet light. For peroxydisulfate, they determined the quantum yield, $\phi(S_2O_8^{2-})$, to be 0.79, and the rate constant to be about 5×10^{-5} s^{-1}, using monochromatic light with λ = 253.7 nm. More recently, Kanakaraj and Marumaruthu[13] reviewed a number of articles and settled on a typical figure of $\phi(S_2O_8^{2-}) \approx 0.68$. Photolysis of peroxymonosulfate causes cleavage of the peroxy linkage to give $SO_4^{\bullet-}$ and $OH^{\bullet}$. Tsao and Wilmarth reported a very high quantum yield in the presence of peroxydisulfate, indicating long chain decomposition. Possibly $SO_4^{\bullet-}$ radicals from $S_2O_8^{2-}$ were interfering with HSO_5^- decomposition, because Kanakaraj and Maruthamuthu used a fairly pure mixed salt of sulfate and peroxymonosulfate, and obtained $\phi(H_2SO_5)$ over the range 0.68 to 1.15 with increasing $[H_2SO_5]$, $k = 1.68 \times 10^{-3}$ s^{-1}. Radiolysis should have a similar effect, but is unlikely to be practicable on an industrial scale.

Photolysis appears to be a rapid and efficient way of generating active radicals from persulfates. It should greatly increase the rate of chromium oxidation, so it may be the dominant pathway in the laboratory at room temperature. The process was not investigated here, despite the potential advantages, because both sludge solutions and work solutions absorb strongly in the near UV. The sludge separation described in Chapter 4 produces chromic hydroxide, which could be dissolved in sulfuric acid to give chromic sulfate solution, which would be less opaque. If that process were of commercial interest, further work in this area would be strongly recommended.

It has been shown that persulfate oxidation of chromium (III) solutions is a complex and poorly understood process. Undesirable side reactions result with increasing acidity, temperature, $[S_2O_8^{2-}]$:$[Cr^{III}]$ ratio, or concentrations of a number of transition metal ions, or when the chromium (III) is already complexed to a strongly coordinating anion. Oxygen is one byproduct, probably accompanied by hydrogen peroxide which reduces the chromium (VI) product. In some conditions there will be no net oxidation at all. A general quantitative model of the reaction is well advanced, but cannot be completed without a lot of kinetic data that is simply not available at present.

Chemical oxidation in practice

It is not practical to dilute work solutions or even sludge solutions to the extent required to minimise inhibition by arsenate. The only possibility is extraction of chromium (III) from sludge with hydroxide [Ch. 4] followed by redissolving in acid and adding persulfate. The undesirable acid-catalysed decomposition cannot be allowed to take over, so base would have to be added carefully throughout the reaction. The oxidation will take days or even weeks at medium heat, consuming vast amounts of power. So the reaction must be completed quickly or not heated at all. Unfortunately, simple experiments show that neither extreme is satisfactory. Side reactions dominate at boiling point, while the reaction literally takes years at ambient temperature.

15.4 g $CrK(SO_4)_2{\cdot}12H_2O$ was dissolved in 150 mL distilled water to give a 0.206 M solution. It was simmered with slow addition of 11.0 g $Na_2S_2O_8$ and 8.6 g commercial grade CuO over about half an hour. The colour change clearly indicated that reaction was nowhere near complete, and considerable gas evolution was noted. It was estimated from UV spectra of a tenfold diluted solution that the extent of reaction was less than 50%. In another simple experiment, one equivalent $Na_2S_2O_8$ was added to 15 mM Cr^{III} and stored in a sealed container kept on the laboratory bench. Base was never added. After a year or so, the reaction was visibly close to complete. Interestingly, this is very much faster than predicted by Eqn. 5.3. Possibly the equation is being extrapolated too far, but more likely photolysis by ambient light is responsible. If it were absolutely necessary to use persulfate, further study of photolysis would be strongly recommended.

In any case, to make a kilogram of sodium dichromate from the appropriate amount of chromium (III) requires 2.73 kilograms of sodium persulfate even if side reactions can be eliminated. In early 1996, quoted prices per kilogram for delivery to FTP's plant at Wiri, Auckland, were $1.75 and $2.16 respectively, so the reagent is at best 3.4 times more expensive than the product. Solubilisation in chromic acid adds little extra cost, while acidity control using copper oxide is free- Cu^{II} would have to be added eventually to make CCA, and copper oxide and copper sulfate pentahydrate are currently identically priced per unit of copper. But photolysis or silver catalysis would increase the price substantially; commercial grade silver nitrate is $240 a kilogram. Disposal costs for chromium hydroxides are unlikely to compete.

In conclusion, chemical oxidation appears to be an impractical method of disposing of green sludge. While the persulfate process can be made to work, it is too uneconomic and inconvenient to be of great interest to the industry at this stage.

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6 Electrochemical oxidation

Electrochemical regeneration of chromium (VI) is well known. The chromic acid electrolyte used in chrome plating and other industrial electrochemical processes, such as indirect electrosynthesis[1], is regenerated from the chromium (III) byproduct at the anodes, according to

6.1 $$Cr^{III} + 4H_2O \xrightarrow{PbO_2} HCrO_4^- + 7H^+ + 3e^- \quad E^{\varnothing}_{red} = 1.35V \; vs \; SHE$$

Lead anodes are used because the overpotential for chromium (III) oxidation is relatively low on a lead dioxide film. Otherwise, oxygen generation

6.2 $$2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \quad (1.23V)$$

would dominate and the process would be very inefficient. There is one condition, that current density be kept high enough to avoid formation of lead chromate, which fouls the electrode.

In this context of CCA waste remediation, there are serious problems with simple electrochemical cell designs. The reverse reaction

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O \quad 1.23V$$

will readily occur at the cathode. It will be difficult to make the resulting equilibrium favour chromium (VI), let alone achieve complete conversion.

The problem is greatly aggravated in the presence of arsenic, since[2]

$$H_3AsO_4 + 2H^+ + 2e^- \longrightarrow HAsO_2 + 2H_2O \quad 0.56V$$
$$H_2AsO_4^- + 3H^+ + 2e^- \longrightarrow HAsO_2 + 2H_2O \quad 0.67V$$

The arsenic (III) product can easily be reduced further, coating the cathode with metallic arsenic,

$$HAsO_2 + 3H^+ + 3e^- \longrightarrow \alpha - As + 2H_2O \quad 0.25V$$

Then highly toxic arsine gas can be given off, admittedly with low efficiency[2],

$$\alpha - As_{(s)} + 3H^+ + 3e^- \longrightarrow AsH_{3(g)} \quad -0.61V$$

Both problems might be solved by dividing the cell with a selectively permeable membrane such as Du Pont's Nafion®. Nafion is a copolymer of tetrafluoroethene and perfluoro[4-(2-sulfonylethoxy)pent-1-ene] in a ratio of 7:1, rather similar to Teflon®. Thanks to the sulfonate groups, it is permeable to cations and solvent molecules, but not to anions such as $HCrO_4^-$ and $H_2AsO_4^-$. It also has the desirable properties of high wet strength and excellent resistance to chemical attack or "poisoning" by contaminants. It is readily obtainable in a variety of sizes and thicknesses and can be reinforced with Teflon.

The cathodic process then becomes

6.3 $2H^+ + 2e^- \longrightarrow H_{2(g)} \quad 0V$

Evolution of hydrogen from one electrode and oxygen from the other is a little dangerous, although it raises the possibility of offsetting power costs by combusting the two in some controlled way. Hydrogen ion is generated faster by either Eqn. 6.1 or 6.2 than it is consumed in 6.3, and it can readily migrate across the membrane, so acidity in the cell must actually increase over time.

Accordingly a bench scale electrochemical cell was constructed [Fig. 6.1]

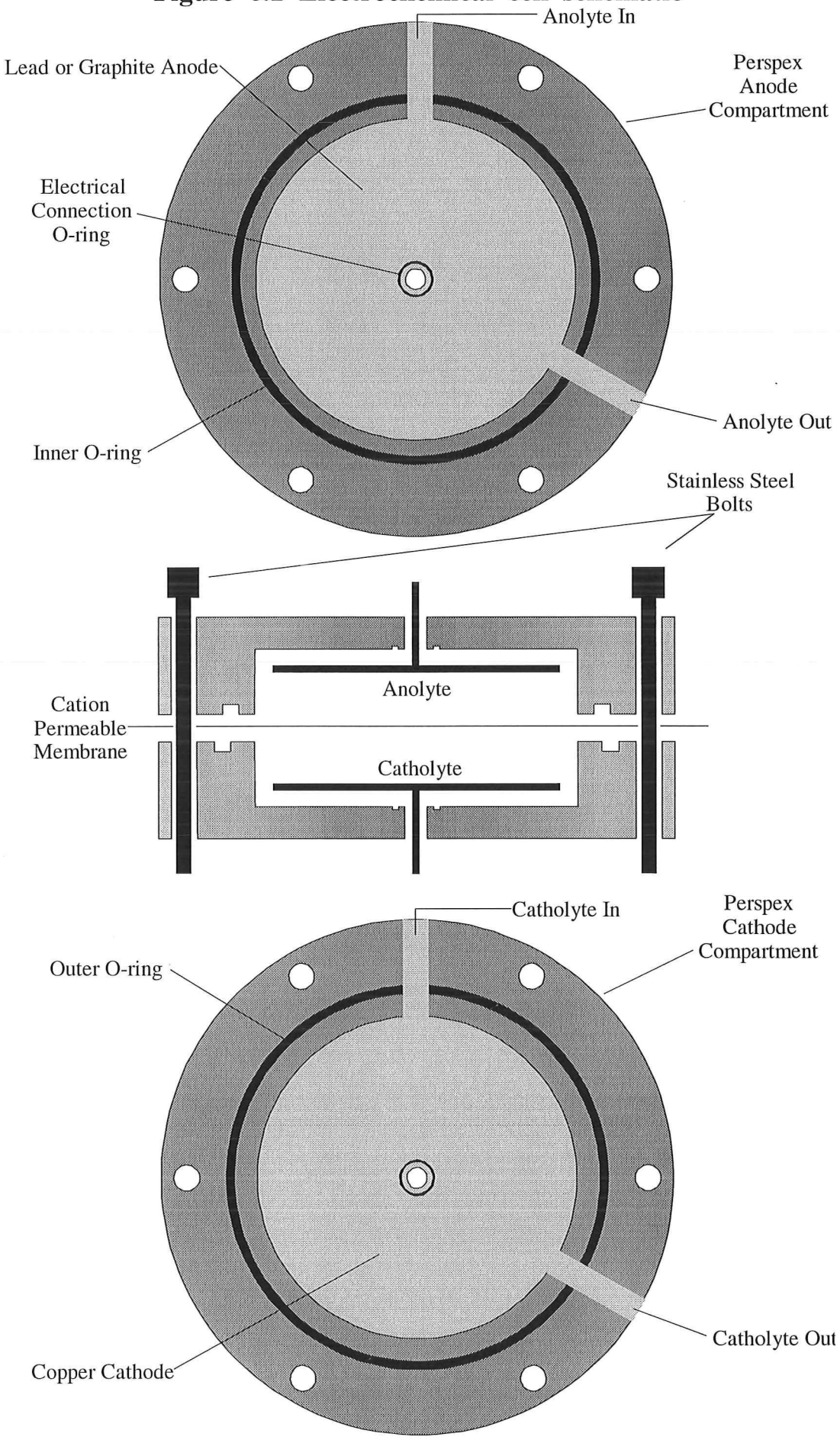
The body of the cell was made from perspex, turned to the desired shape on a lathe. The end plates were glued to the cylindrical walls with Araldite, making two 39 mL half cells with the membrane sandwiched in between. 5 mm bolts pass right through all three and allow the cell to be assembled or disassembled conveniently. A hexagonal arrangement ensured that the O-rings were properly compressed, there was no leaking around the membrane. Later it was found that the bolts had to be stainless steel or they quickly rusted. The inlet and outlet tubes were $^1/_4$" PVC, jammed in hot, glued with Araldite, and cut off flush on the inside.

The cathode was cut from sheet copper, weighed, and attached to the centre of the end plate with a 4 mm stainless steel screw, whose other end was connected to the electrical circuit by a crocodile clip. A small O-ring was fitted between the electrode and the end plate to seal the opening. The lead anode was made and attached in the same way; thickness varied between 1.3 and 2.0 mm. The screw was encouraged to sink into the soft lead, because it improved the seal around the electrical junction and minimized the proportion of the surface in steel rather than lead dioxide. Tinning over the screw head was ineffective because the solder gradually dissolved when the cell was operating. To provide the correct surface in accordance with electroplating guidelines[3], the lead was anodized at ca. 3 V, 1.2 A, for some hours in 200 gL^{-1} warm CrO_3, which gave a fairly even coating of chocolate-coloured lead dioxide. In later experiments, a graphite anode of similar dimensions was sawn out of a large graphite block and attached in the same way.

Current was supplied by a DC generator running off mains power, which was supposed to generate 4 A at 2, 6, or 12V. The actual voltage and current across the cell was measured by appropriately connected Dick Smith Electronics Q-1419 and -1420 digital multimeters reading '$3^1/_2$' significant figures. A slidewire was added to the circuit to enable further tuning of voltage and current, although the cell response was rarely ohmic.

Because it would have taken several months and nearly a thousand dollars to acquire a peristaltic pump for the electrolytes, car windscreen wiper pumps were substituted. While they were not designed to run continuously for over a minute without overheating, they cost less than $25 each off the shelf, took the correct size of tubing, filled or emptied the compartments quickly, and ran happily off the generator.

Figure 6.1 Electrochemical cell schematic



Since it is difficult to extrapolate electrochemical results from bench scale to industrial scale[1], qualitative aspects of the reaction were of most interest. The extent of reaction could be estimated from colour changes toward the bright orange of dichromate solution; similarly, any colour change in the electrodes or the acid catholyte was significant.

The first experiments used a chromium (III) potassium sulfate anolyte and a dilute sulfuric acid catholyte. Not only did this cell prove effective, it appeared that complete oxidation could be achieved with sufficiently long reaction times. Applying a potential of around 2.3 V yielded a current of around 0.1 A, which was able to effect a considerable colour change over about an hour.

Let the efficiency of the cell be ε, defined as the proportion of charge passed through the cell which goes toward oxidising chromium (VI);

$$\textbf{6.4} \qquad \varepsilon \equiv \frac{-3\Delta\left(Cr^{III}\right)}{\frac{VIt}{F}}$$

where $\Delta(Cr^{III})$ is the change in moles of chromium (III) during the running time t, V is the voltage across the cell and I the current through it, and F is Faraday's constant, 96.485 $kCmol^{-1}$.

For these experiments, ε was estimated at 80%, a remarkably high number considering electroplating efficiencies typically fall into the 8-18% range[3]. This figure is supported by the observation that gas was evolved from the cathode, but not obviously from the anode.

A blue colour in the catholyte turned out to be chromium (III) which had migrated through the membrane. This is unlikely to be reduced further;

$$Cr^{3+} + e^{-} \longrightarrow Cr^{2+} \quad -0.407V$$
$$Cr^{3+} + 3e^{-} \longrightarrow Cr \quad -0.744V$$

Since the used catholyte solution contained the same species as the original anolyte, it could be transferred to the anode compartment for oxidation whenever chromium (III) built up. For these reasons, this migration was not considered to be a problem.

One concern was the buildup of lead chromate on the anode surface. As expected[3], this degradation seriously inhibited the flow of current over a period of several experiments. In chrome plating, lead anodes are operated at more than 8 Adm^{-2} in warm solutions, especially when new. This anode was only getting about 0.5 Adm^{-2} at room temperature, not enough to maintain the lead dioxide layer. Cold chromate solution degrades the anode surface even when the current is off, so it is most inadvisable to leave the anolyte in the cell. During any single one of these initial experiments, the current was also observed to decay during the run, and to be proportional to the amount of solution in the anode compartment.

The next set of experiments involved oxidation of a 1:1 mixture of 3% CCA sulfate and 45 gL^{-1} $CrK(SO_4)_2 \cdot 12H_2O$, 0.09M in both Cr^{VI} and Cr^{III}. Voltage was 2.6 V and initial current was 0.19 A. The standard FTP quality control titrimetric method for chromium (VI)[4] was employed in an attempt to quantify the extent of reaction. Ferrous ammonium sulfate reductant and sodium diphenylaminesulfonate indicator are added to the dilute sample, which is then back-titrated with acidified sodium dichromate until a sharp colour change from green to purple:

Table 6.1 First quantitative results

t (min)	$[Cr^{VI}]$ (M)	ε (%)
0	0.095	-
30	0.11	30
45	0.12	35
60	0.12	20
90	0.13	25
180	Appears complete	15

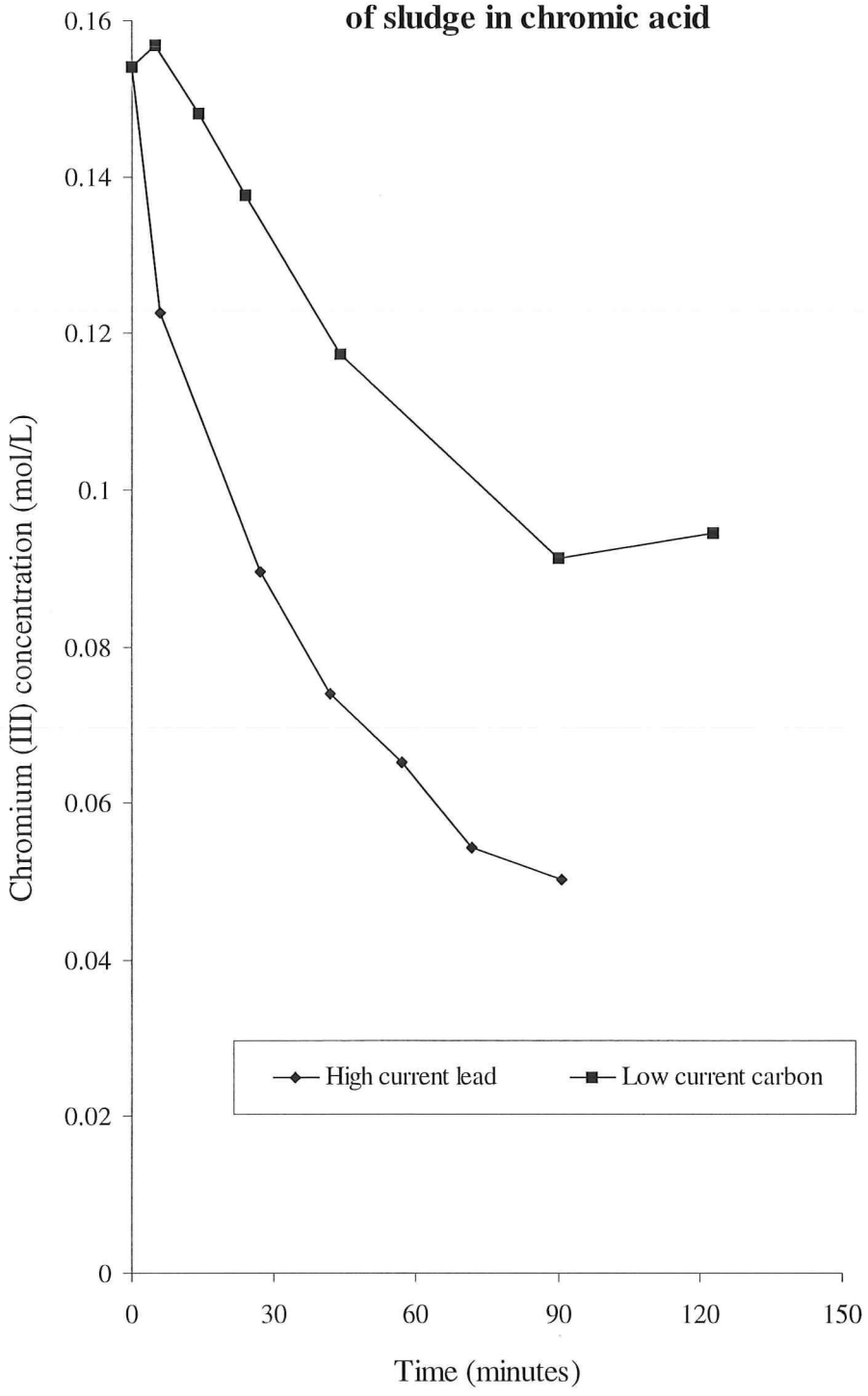
The inaccuracies in these determinations were painfully high, and the anode exhibited unacceptable decay. Therefore the anode was reconditioned and the experiment was repeated at a higher current and voltage, 1.0 A at 6 V. Since low voltages are desirable in order to favour Rxn. 6.1 as much as possible, a graphite electrode was trialled at the original 0.20 A, requiring 4 V. Both electrodes came through the following trial unscathed.

The substrate was also modified to better reflect a likely industrial situation. To minimise the introduction of sulfate [cf. Ch. 3], chromic acid was used to dissolve the sludge. This was deemed more appropriate than arsenic acid because a smaller volume is necessary, it seemed less likely to inhibit oxidation, and any reduction of the added chromium (VI) would be rapidly countered.

A 50 $g.L^{-1}$ sludge solution was prepared by adding 0.5 mL concentrated sulfuric acid to 5 g sludge [Ch. 2] and then a twofold excess [cf. Ch. 3] of chromic acid, 5.0 g in ca. 50 mL distilled water; the solution was boiled for half an hour, cooled, filtered, and made up to 100 mL.

The course of the reaction was followed using ultraviolet-visible absorption spectroscopy. A number of small aliquots were taken from the anolyte using a Pasteur pipette, then 0.50 mL was taken from each aliquot, diluted to 3.0 mL with distilled water, and its absorption between 400 and 800 nm measured on a Hewlett-Packard HP8452A diode array UV spectrophotometer. Since the chromium (III) peak at 586 nm might easily have been affected by the massive chromium (VI) peak at 350 nm, the wavelength at half-height, 655 nm, was used for quantitation. After allowing for abstraction of the aliquots, the following results were calculated:

Figure 6.2
Electrochemical oxidation of sludge in chromic acid



Both curves look like exponential decays, suggesting a general rate expression

$$\mathbf{6.5} \qquad \frac{d}{dt}\left[Cr^{III}\right] = -k\left[Cr^{III}\right]$$

In which case, for the high current lead experiment k = 2.1 × 10^{-4} s^{-1}, $t_{90\%}$ = 190 min., which gives ε = 9% for 90% conversion; for the low current carbon experiment, k = 9.6 × 10^{-5} s^{-1}, t_{90} = 400 min., ε = 21% for 90% conversion, confirming the advantages of a relatively low voltage.

Commercial plating is conducted at around 40 °C, and there are several arguments for heating this cell. Firstly, it appears to help maintenance of the lead dioxide surface. It might then be possible to run the cell at a lower voltage, which should increase the cell efficiency, and therefore profitability. Heat increases the lability of chromium (III) compounds, and the rates of transport around the compartment or through the membrane; these are all factors which may hinder chromium oxidation, possibly depending on cell design. The interplay of such factors makes it difficult to predict the exact effect scale-up on an electrochemical process.

This cell consumes electricity and generates chromium (VI). Let the price of one mole of electrons be p_e, one mole of chromium (VI) p_{Cr}, and the economic return of the process be π,

$$p_e = \frac{FVP_e}{3.6 \times 10^6}, \qquad p_{Cr} = \frac{M_R P_{Cr}}{1000n}, \qquad \pi = \tfrac{1}{3}\varepsilon\frac{p_{Cr}}{p_e}$$

$$\mathbf{6.6} \qquad \pi = \frac{1200\varepsilon M_R P_{Cr}}{FP_eV}$$

where P_{Cr} is the price of a kilogram of the chromium (VI) salt, M_R is its molar mass, n the number of chromium atoms per molecule, F is Faraday's constant, P_e is the price of one kilowatt-hour of electricity, and V is the voltage across the cell. The current New Zealand commercial cost of electricity is only *ca.* \$0.15 $(kWhr)^{-1}$; chromic acid is M_R 99.99 $gmol^{-1}$ and costs FTP \$3.16 kg^{-1}; F is 96.485 $kCmol^{-1}$: therefore the break-even point π = 1 requires ε to be 15% at 4.5 V, 23% at 6 V. The low current experiment with carbon anode was profitable, but the high current lead experiment was not, nor was the low current lead experiment [Table 6.2].

This expression for π is by no means complete. The cell also disposes of sludge, and requires operation, maintenance, and consumables. The current landfilling cost of sludge is more than five times its chromium value [Ch. 5] and can be incorporated into the model simply by increasing P_{Cr} by the same factor. On the other hand, there will be a solubilization cost which will decrease P_{Cr} slightly. Nonetheless, oxidation on a lead anode appears decidedly economic when this is taken into account. Consumables, such as electrodes, membranes, replacement catholyte, should not be estimated from results on this bench cell, particularly since it was not tested to failure of any component. Similarly, these experiments have not generated sufficient data to estimate heating costs, should that become advisable. There may also be disposal costs for wastes, such as the finely divided metals produced at the cathode.

Nonetheless it appears from the analysis that it may actually be cheaper to make dichromate from chromium (III) wastes than to buy it. It would be most interesting to experiment with spent tanning wastes, for example, which contain chromium (III) and a heavy load of fats, proteins, and other organic material.

In none of these experiments were deposits of amorphous elemental arsenic ever observed on the cathode, nor was the strong garlic odor of arsines ever noticed. It seems, therefore, that arsenic migration across the membrane is insignificant. Nonetheless, an arsine detector would be most advisable in any scaled-up cell, in case of membrane failure.

Copper (II) is certainly being transported into the cathode compartment, because a reddish-black precipitate consistent with finely divided metallic copper is observed. The extent of transport is hard to quantify at this stage. While this process is no doubt accelerated by the electrostatic attraction of cations to the cathode, the possibility of excessive copper depletion is a further reason not to leave anolyte sitting in the cell. Iron (III) must also be transported and reduced, though probably not to the metal;

$$Cu^{2+} + 2e^- \longrightarrow Cu \quad 0.34V$$

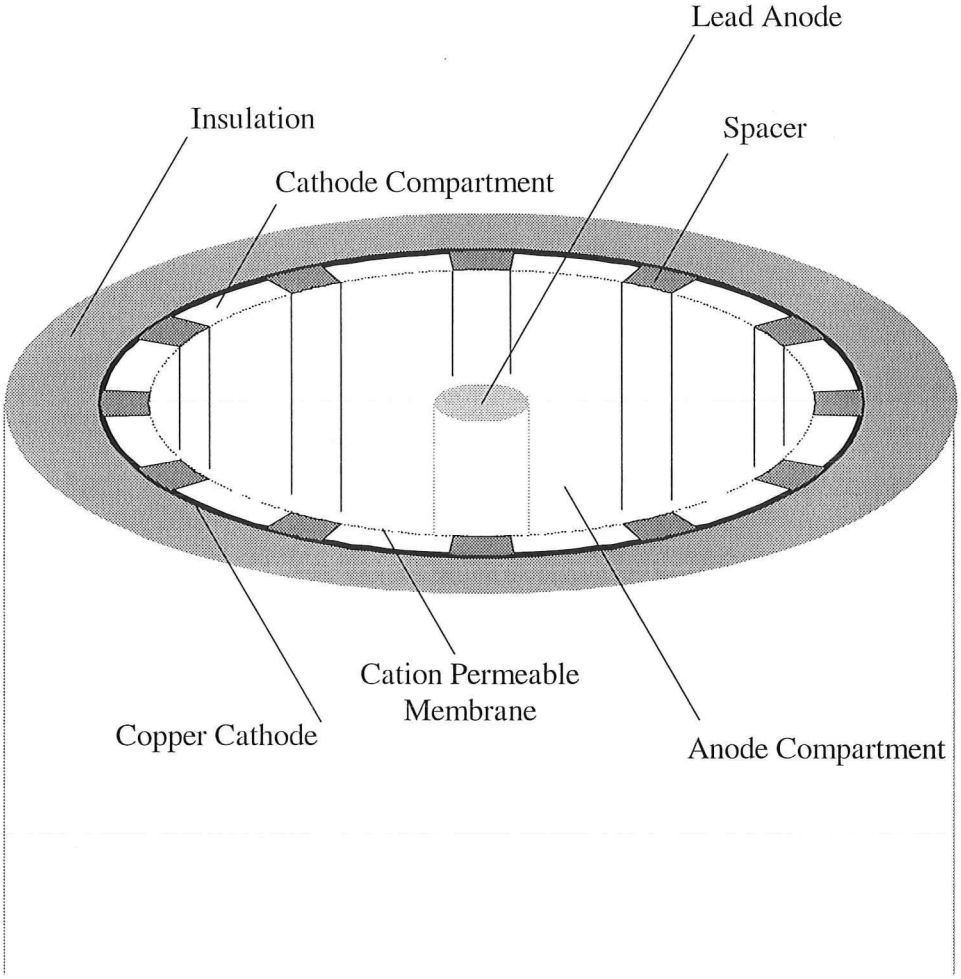
$$Fe^{3+} + e^- \longrightarrow Fe^{2+} \quad 0.77V$$

$$Fe^{3+} + 3e^- \longrightarrow Fe \quad -0.04V$$

$$Fe^{2+} + 2e^- \longrightarrow Fe \quad -0.45V$$

A number of improvements to the cell design can be suggested. If current density on the anode is critical, anode area should be minimized, and the cell should be heated. While the volume of the cathode compartment should also be minimized, so that relatively small proportions of cations migrate to the catholyte, the membrane area should be maximised so that transport between compartments does not become rate-limiting. The shape which best fits these requirements is a cylinder:

Figure 6.3 Proposed design for next generation cell



The separator between the cathode and the membrane must permit catholyte solution and hydrogen gas bubbles to move freely through the cathode compartment. Simple axial strips is one possible arrangement, a helix is another. The anode, containing a supporting material must go down the centre of the cylinder, or potential distribution will be uneven. Heating elements could be included in the insulation or immersed in the anolyte. Theoretically, there is no reason why the cylinder could not be twisted into a spiral, or any other convenient shape, so long as cross-sectional symmetry is preserved and there are no internal points or edges.

Alternative electrode materials may be desirable. Carbon or titanium anodes may cause some inefficiency due to the overpotential problem, but may be much more durable than lead. The cathode was made of copper because it was originally assumed that any copper in the catholyte would plate out on the electrode surface. Since this does not seem to be the case, there are many alternatives. A cathode material which selectively reduced hydrogen ion in preference to copper cations would be ideal. The cathode might also benefit from a more finely divided surface.

It was concluded in Chapter 2 that there is a window of opportunity between timber treatment and the end of sludging, when some or all of the chromium (III) could be oxidised or removed. However, it would be difficult to apply this method to the situation. A small increase in acidity on electrolysing would be good, but a large increase would not. There would be some undesirable copper depletion, aggravated in CCA where the relative copper concentration is substantially higher. Heating would have to be avoided because it would accelerate sludging. The cell would have to cope with thousands of litres of work solution which would probably contain foreign matter. The average timber treatment company would have little understanding of the process, or of the things which might go wrong with it, such as arsine evolution following membrane failure. Still, it might be of interest to a really large facility.

Finally, note that this process is quite different from the electrodialytic technique applied by Ribeiro et al.[5] *to a CCA contaminated soil. Their electric current was not intended to oxidise chromium (III), but to persuade charged CCA species to move through the soil toward the electrodes. Indeed chromic ion, being positively charged, moved toward the cathode. The interposition of a cation exchange membrane between the contaminated soil and the cathode compartment allowed the removal of the migrating species into a different medium, rather than protecting fully oxidised species from reduction. Thus they also used an anion exchange membrane between the soil and the anode compartment.*

An electrochemical cell capable of completely oxidising chromium (III) to chromium (VI) has been designed and trialled at bench scale. The process is cheap and avoids significant undesirable side reactions. It appears to be an effective method of remediating spent CCA waste.

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7 CCA in wood

Possible CCA fixation products

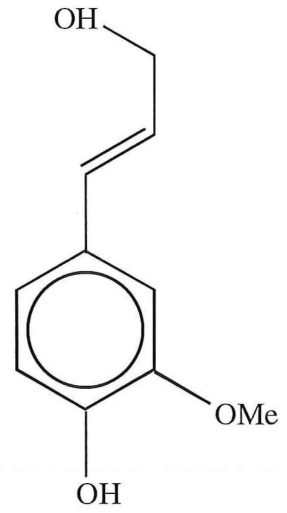
The reactions which cause CCA components to fix strongly into wood must include the sludging processes detailed in Chapter 2. Following Hartford[1], sludging is "as a first approximation, fixation which takes place outside the wood". However, since the wood cell structure isolates the fixation reactions from the strong buffering action of the bulk solution, the pH can change faster and further. Using a flat membrane glass electrode, Dahlgren and Hartford[2,3,4,5] recorded pH up to 5.5 in wood during CCA treatment. Such low acidity will not only precipitate chromium (III) arsenate, but also copper (II) arsenate and hydroxides and chromates of both metals.

Chromates can be eliminated because chromium (VI) is definitely not present in fully fixed timber. This is usually demonstrated with a chromotropic acid spot test. Also, Kaldas and Cooper[6] have presented chromium-2*p* XPS results showing complete conversion to chromium (III).

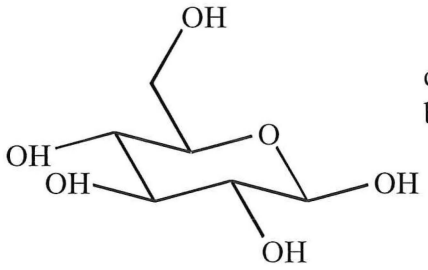
A number of authors have used electron spin resonance spectroscopy (ESR or EPR) to show that trace metastable chromium (V) intermediates can persist for up to six months[7,8]. Chromium (V) is a common intermediate in the reduction of chromium (VI) by organic species[9]. It is interesting that chromium (IV) is not observed, since the blue $Cr^{IV}O(O_2)_2$ is one intermediate in the room temperature reaction between hydrogen peroxide and acidified dichromate[10]. This may invalidate Dahlgren and Hartford's comparison between fixation and peroxide reduction of CCA[5]. On the other hand, chromium (IV) is an even stronger oxidant than chromium (V) and may simply decompose more quickly.

In type I CCA, the active elements are present in the ratio 2.0 Cr: 0.9 Cu: 1 As. There are not enough arsenate groups to complex all the chromium (III) and copper (II); if fixation consisted of depositing sludge on the wood cell walls [Ch. 2], over half the chromium and 80% of the copper would remain unbound. Either this remainder would form hydroxides, or else it would interact with the wood matrix. What forms could such an interaction take?

Chemically speaking, wood is a highly structured composite of two polymers, lignin and cellulose; long chain heteropolysaccharides collectively called hemicellulose; and a wide array of derivatives and associated minor compounds. Cellulose and hemicellulose are grouped under the class of carbohydrates.

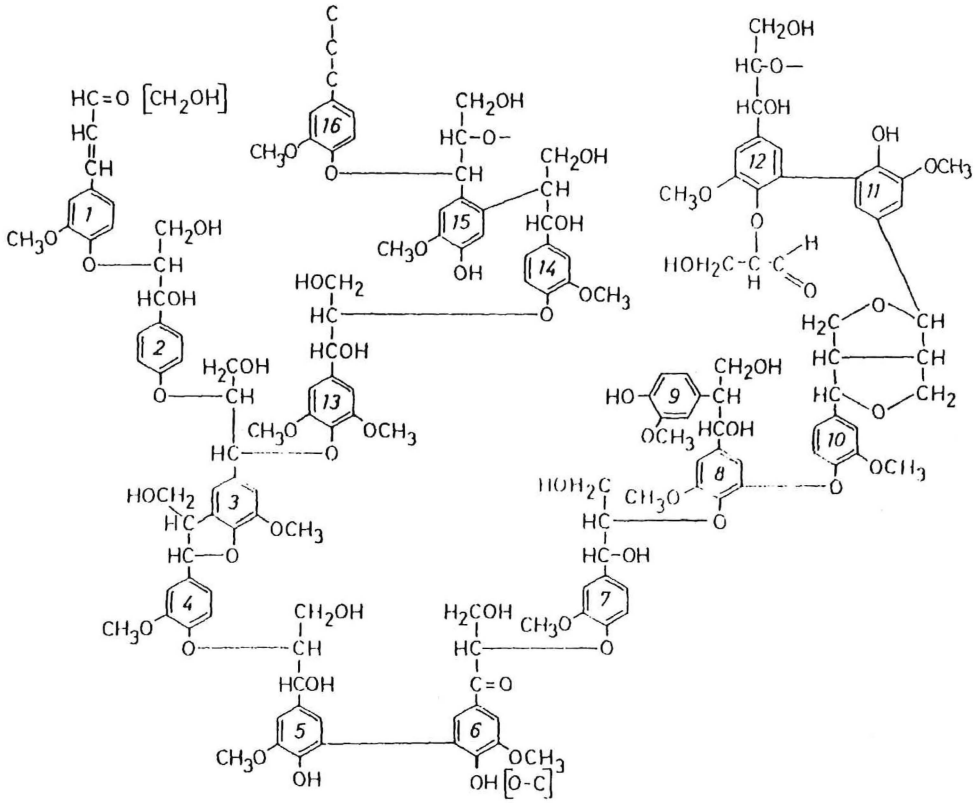


'Coniferyl alcohol', 4-(3-Hydroxy-1-propenyl)-2-methoxyphenol, the principal precursor of lignin. Some units lack the methoxyl group ('*p*-coumaryl alcohol'), or have a second at the 6- position ('sinapyl alcohol'). A generalised structure for lignin is shown in Fig. 7.1.



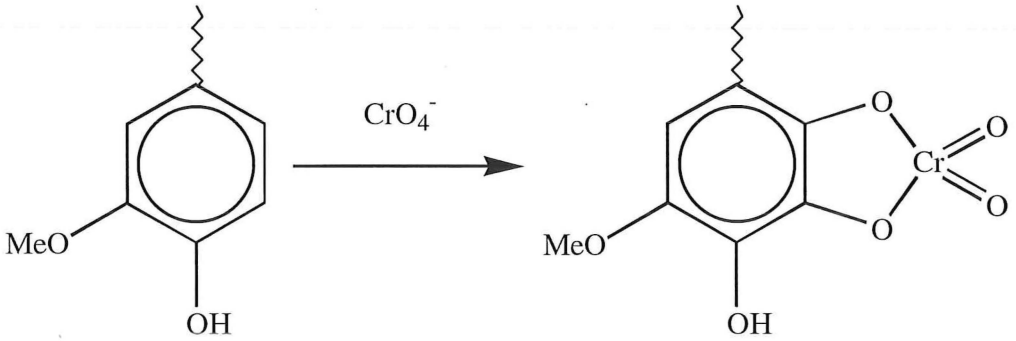
β-D-Glucopyranose, which forms cellulose when linked by 1→4 glycosidic bonds.

Figure 7.1 Structure scheme for a general softwood lignin [10]

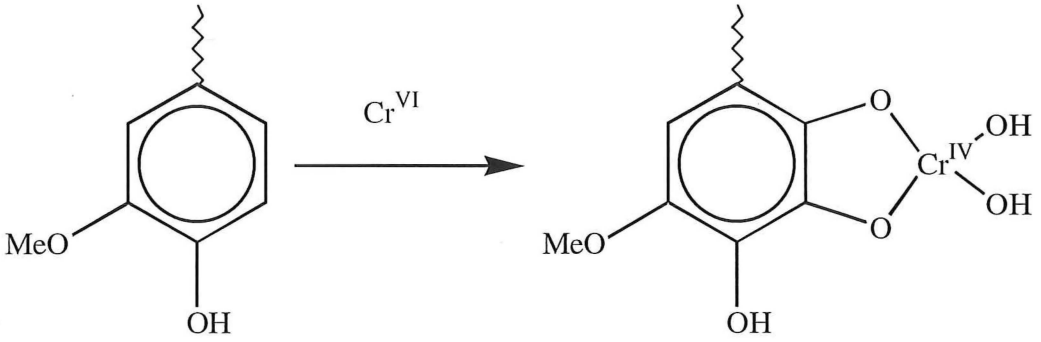


Hughes[8] has shown that both lignin and carbohydrates will reduce chromium (III), although fixation is better on whole wood. This suggests that extractives are also involved. Wood does become slightly more brittle when treated, which is consistent with the removal or destruction of lubricant extractives. Cleavage of polymer chains would result in a much greater loss of mechanical strength[1].

Ostmeyer *et al.*[11] observed that CCA treatment caused a relative decrease in the part of the infrared spectrum due to aromatic ring vibrations. They proposed that chromic acid could form a stable ester with the aromatic rings of lignin:

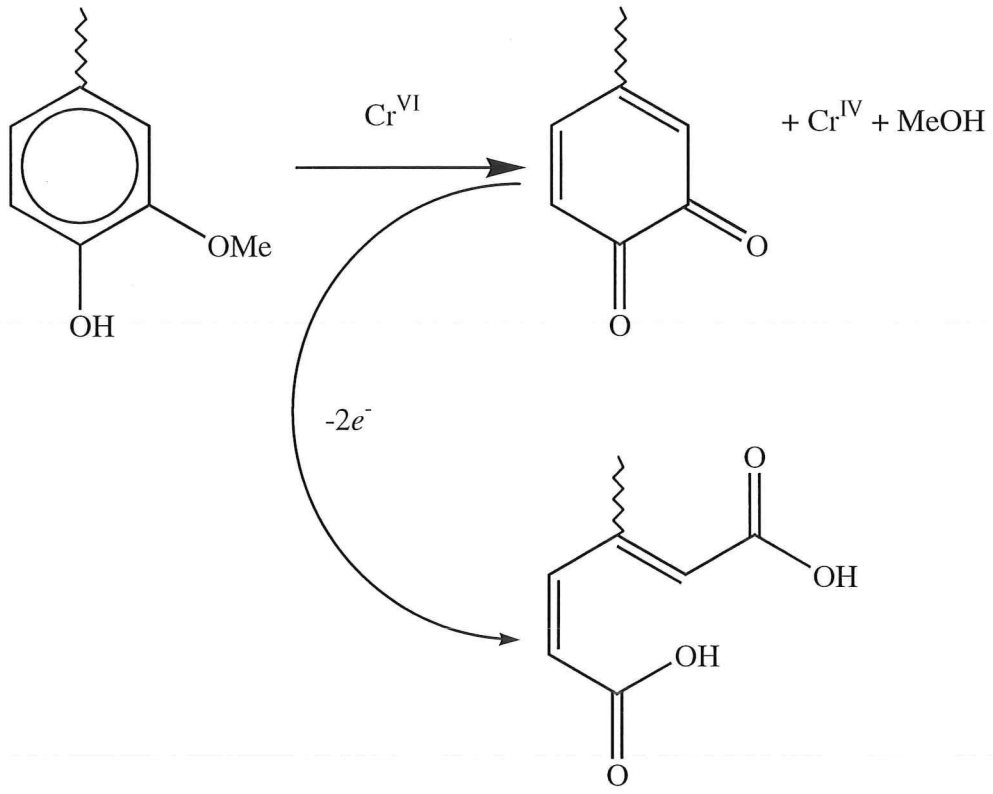


But the reaction is an oxidative attack, displacing two hydrogen ions. It should be written



which highlights the instability of the proposed product. Chromium (IV) has never been observed in ESR studies[8].

More plausibly, abstraction of an electron from the hydroxy group will lead to a stable *o*-quinonoid, which might even oxidise further to a muconic acid structure;

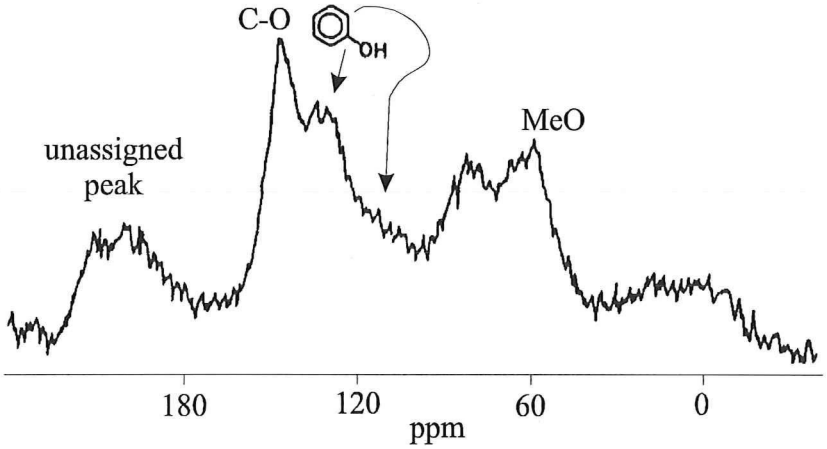


This reaction has been observed in the oxidation of guaiacol (2-methoxyphenol) by permanganate or periodate[12], and in the chlorine dioxide stage of lignin bleaching. The standard potential for a related reaction, the reduction of benzoquinone to catechol, is only 0.7V. That is substantially less than the standard chromate reduction potential of 1.35V, so this reaction can be expected to proceed readily. Since benzoquinone has a peak in the relevant region of the infrared spectrum, but muconic acid does not[13], the change in the infrared spectrum is probably due to cleavage of the aromatic rings.

Permanganate, periodate, and chlorine dioxide all proceed to attack the propyl part of the base unit, leading to depolymerisation and solubilisation of the lignin. Indeed, if the hydroxyl group is protected by methylation, the propyl chain is attacked preferentially[2]. However, since the physical properties of wood are not compromised by CCA treatment, either chromate is incapable of degradative oxidation under these conditions, or the reaction does not reach that point in practice.

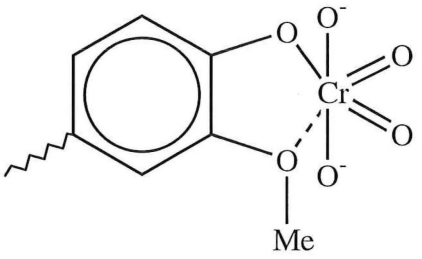
In an attempt to support Ostmeyer *et al.*'s chromic ester hypothesis, Pizzi[14] reacted guaiacol with chromate and analysed the resulting precipitate by ^{13}C NMR, obtaining the following spectrum [Fig. 7.2];

Figure 7.2 ^{13}C NMR of guaiacol-chromate reaction product [14]

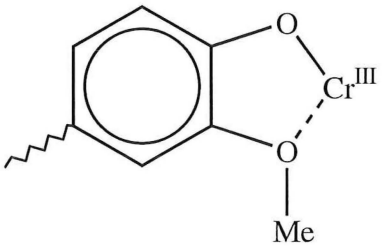


He concluded that the shift of the 6-carbon signal from its usual place at around 110 ppm was due to the formation of the chromic ester. But the spectrum as a whole is more consistent with partial conversion to muconic acid, which explains the substantial peak that has appeared at around 200 ppm.

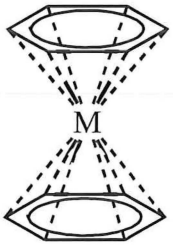
Pizzi carried out molecular modelling calculations optimizing non-bonded interactions, and proposed three further types of chromium-lignin complexes on that basis;



"type 2"



"type 3"



"type 4": M = Cr^{3+} or CrO_4^{2-}

Pizzi's type 2 and 4 complexes can be eliminated out of hand. As written, the type 2 complex involves chromium (VII). Since this is quite impossible, one of the oxo donors should probably be changed to a hydroxo group. But that still gives 6-coordinate chromium (VI), which is equally implausible. In any case, like the type 4 chromium (VI) complex it requires an anion to be attracted to a δ-negative region of the molecule. Pizzi's calculations appear inconsistent with elementary electrostatic considerations.

Pizzi's claim that the type 4 chromium (III) complex is similar to ferrocene is not readily apparent. Ferrocene is bis(cyclopentadienyl)iron (II). The aromatic radical anions are stabilised by donation from the π system into the valence shell of the cation. The eighteen electrons, six π from each ring and six 3*d* from the metal, neatly fill the nine bonding orbitals. There is no such mutual advantage in the 15-electron system of d^3 chromium (III) and two 6π substituted benzenes. Dibenzenechromium (0) does obey the 18-electron rule, but it cannot form in these conditions, nor is it stable to aromatic substitution.

The type 3 interaction, coordination of chromium (III) to a phenolate, is much more sensible. However, the pK_a of phenols is substantially higher than that of carboxylic acids, making it relatively difficult for metals to displace hydrogen ion at low pH. While basic copper preservatives appear to bind to phenolates, this is unlikely in acid preservatives like CCA[8].

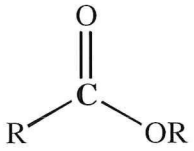
Copper (II) and chromium (III) could readily bind to carboxylates at these acidities. There are some carboxylate residues in hemicellulose, and the muconic acid hypothesised earlier is a carboxylic acid. But a better source is primary alcohol groups, which will readily react with chromium (VI) to give carboxylic acids. Primary alcohols are plentiful in both lignin [Fig. 7.1] and carbohydrates. They must be terminal to chains, therefore relatively accessible. It also follows that their oxidation does not change the backbone of the chain significantly.

Ostmeyer et al.[11] also suggested that chromium (VI) might oxidise propenyl chains in the lignin, presumably yielding a secondary alcohol. However, double bonds are relatively rare in softwood lignin [Fig. 1] and slightly less accessible than primary alcohols. While this reaction appears quite feasible, it is unlikely to contribute much to fixation.

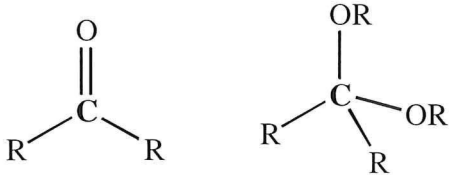
A number of workers[6,15,16] have attempted to use X-ray photoelectron spectroscopy (XPS) to observe chemical changes of the wood during fixation. XPS carbon-1s spectra show separable peaks for carbon-containing groups, depending on the number of carbon-oxygen bonds [Fig. 7.3], so it was thought that the technique would shed some light on the oxidation of wood by chromium (VI), and therefore the fixation products. Unfortunately, the results have been very inconsistent, and the reported C1:C2 ratios are generally much higher than would be expected. Ruddick et al.[16] hypothesised that migration of C1- rich extractives toward the surface of the wood during soaking and drying compromises XPS analysis. The sampling depth for XPS is only a few nanometres, which makes the technique extremely vulnerable to surface effects.

Kaldas and Cooper[6] also observed a massive drop in C4 peak area, indicating loss of carboxyl groups through acid-catalysed decarboxylation. However, this is unlikely to occur in practice. Their exposure of thin wood slices to a vast excess of bulk CCA must have maintained solution acidity at a much higher level than normal.

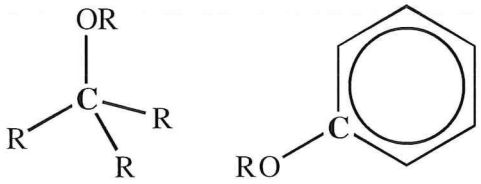
Figure 7.3 Differentiation of functional groups by C1*s* XPS



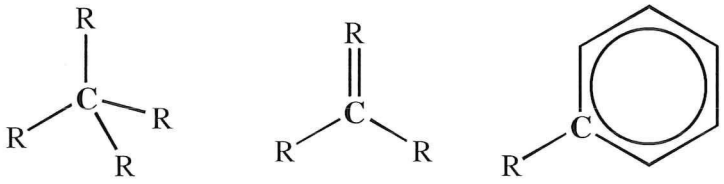
C4 peak: carboxyls



C3: carbonyls, acetals, etc.



C2: alcohols and ethers



C1: unsubstituted alkanes, alkenes, and aromatic rings

The experiments of Pizzi et al.[17] to determine distribution of preservative on lignin or holocellulose fractions are not helpful in determining the nature of the fixation products. The reagents used to separate the fractions appear to include strong sulfuric acid, which will certainly solubilize any purely inorganic CCA fixation products, and probably break up any wood-metal ion complexes too[18]. Therefore the results cannot be representative. Since wood is a closely linked copolymer, with some bonding between the carbohydrate and lignin, even the concept of distribution does not seem particularly useful.

Since ligand exchange reactions of chromium (III) are extremely slow [Ch. 2, Ch. 5, etc.], chromium (III) will have difficulty competing with copper (II) for the carboxylate binding sites. On the other hand, chromium (III) hydroxide will form relatively rapidly at sufficiently low acidity. It is therefore proposed that **the fixation products of CCA are dominated by chromium (III) arsenate, chromium (III) hydroxide, and wood carboxylate- copper (II) complexes**. In which case, arsenic should be found associated with chromium in treated wood, but copper should be separate from both.

This is consistent with the results of Kazi and Cooper[19], who report that acetic acid, humic acid, EDTA, and lignosulfonic acid could all extract the majority of the copper from treated wood, while leaving most of the chromium and arsenic. Conversely, oxalic acid extracted only 55% of the copper, but almost all of the chromium and arsenic. Similarly, Fox *et al.*[20] observed that the leachability of copper from treated wood increased with decreasing pH, whereas chromium and arsenic were not significantly affected. Pasek and M^{c}Intyre were able to extract a considerable proportion of the copper from CCA contaminated soil using ammonia solution[21]. Ruddick[22] reported selective leaching of copper from treated wood in field tests, possibly due to bacterial action.

To confirm this conclusion, a technique to investigate the association of elements on a molecular scale *in situ* is needed. Magic angle spinning NMR is inappropriate because arsenic and the principal isotope of chromium are NMR inactive, while the principal isotope of copper is a quadrupole nucleus with poor NMR properties. Though X-rays pass easily through wood, the fixation products are not crystalline and so diffraction techniques are impossible. The most appropriate technique is X-ray absorption fine structure spectroscopy (XAFS).

X-ray absorption fine structure spectroscopy of fixation products

When atoms absorb X-rays, they emit electrons from core orbitals. The threshold energies for absorption are equal to the binding energies of those electrons, so that each element has a distinctive X-ray absorption spectrum (XAS). Nearby atoms may back-scatter the photoelectrons, producing periodic oscillations in the XAS somewhat above the absorption edge. These perturbations are called extended X-ray absorption fine structure (XAFS). The amplitudes of the oscillations depend principally on the size and number of the scatterers, and the frequencies are related to the distances between absorber and scatterers. So if all the nuclei of the absorber element are in similar sites, it may be possible to deconvolute the XAFS and thereby identify all the neighbours out to 4 Å or more. Unlike diffraction techniques, long-range order is not required.

According to the proposed model, arsenic predominantly fixes as chromium (III) arsenate. Therefore, we should expect to see chromium (III) nuclei close to arsenic. Conversely, if copper is present in the form of wood carboxylates, there will be no heavy scatterers nearby. Chromium presents more of a problem since multiple sites are expected, both arsenates and hydroxides. It should be difficult to extract meaningful structural information from the chromium XAFS of CCA-treated wood.

Since the XAFS spectrum is only a perturbation of the absorption peak, very intense radiation is required to achieve a sufficiently high signal to noise ratio. Synchrotron radiation is the usual solution. There are no synchrotrons in New Zealand; the nearest XAFS facility was at the Photon Factory in Tsukuba, Japan. Dr. Garry Foran, Project Scientist for the Australian Beamline, very kindly agreed to support a submission to the Photon Factory Steering Committee. Eventually, forty-eight hours of free beamtime were allocated for experiments on treated wood samples. To make full use of this time, Dr. Harland's senior chemistry doctoral student, Claire Vallance, was invited onto the project. Claire's help with collecting and analysing the data was invaluable.

Over 20 samples were originally prepared, but due to time constraints only the high priority samples could be analysed [Table 7.1]. This did not include any chromium XAFS, since the results were expected to be poor and considerable time would have been lost in preparing the equipment for a third element. Nonetheless, each wood sample was run twice, in case any particular data set turned out to be substandard:

Table 7.1 XAFS samples

Type	Subtype	Elements	Mode
Cupric arsenate		Cu, As	Transmission
Sludge		Cu As	Fluorescence Transmission
CCA- treated wood	H4 salt, outer section.	Cu, As	Fluorescence
	H4 salt, middle section	Cu, As	Fluorescence
	H4 salt, inner section	Cu, As	Fluorescence
	H4 oxide, outer	Cu, As	Fluorescence
	H5 oxide, outer	Cu, As	Fluorescence
AC- treated flour	NH_3 formulation	Cu	Fluorescence
	NH_4^+ formulation	Cu	Fluorescence

Cupric arsenate: Commercial sample from FTP. Cu 32.7%, As 32.5%, S 0.354%, Fe 0.043%, moisture 14%. Suspected $Cu_3(AsO_4)_2{\cdot}2CuHAsO_4{\cdot}9H_2O$ *[cf. Ch. 4].*

Sludge: As characterised in Ch. 2.

CCA-treated wood: Oxide-treated wood was bought from Cantapine Ltd., Christchurch, New Zealand, a subsidiary of Goldpine Ltd., New Zealand. It was high-density Pinus radiata from Nelson, New Zealand, nominal diameter 150 mm, treated with Koppers-Hickson's GoldTan® Oxide in accordance with New Zealand Standard MP 3640. Only the outermost stakes, approximately 20 mm in depth, were analysed. Salt-treated P. radiata was bought from Mike Cairns Ltd., Christchurch, New Zealand. The wood came from a similar source and was treated according to the same standard. The roundwood, nominal diameter 100 mm, was profiled from surface to core in three equal intervals of ca. 20 mm.

A board of ca. 25 mm width, including the core, was cut from each log. Unblemished sections were taken from these boards, then cut up along the grain to give stakes representing different depths into the wood. The stakes were milled to sawdust using a table-mounted circular saw with carbide-tipped blade, which ground finely without perceptible heating. This sawdust was collected in plastic bags covering the hopper beneath the blade, and from the tabletop, the apparatus being vacuumed clean between stakes. Then it was air-dried with some mild heating, sifted through a 60 mesh filter, and the resulting dust stored in tightly sealed 14 mL sample vials with Teflon-lined caps.

AC-treated wood flour: Prepared by Dr. Tony Bergervoet, Fernz Timber Protection, Auckland, N.Z. Sawdust was generated from untreated, unblemished Pinus radiata using a table-mounted circular saw with carbide-tipped blade, then passed through a clean domestic kitchen flour mill. The resulting wood flour was treated with two variants of ammoniacal copper preservative (AC) to a nominal retention of 0.75% CuO. The 'NH_3*' solution was 40% ammoniacal cupric carbonate + 9% ammonium bicarbonate - ammonium carbamate double salt. For the '*NH_4^+*' solution, the copper complex was prepared using ammonium bicarbonate instead of ammonia. In either case, it was then sifted and stored as described above.*

Room-temperature X-ray absorption measurements were made on bending-magnet beamline 20B at the Australian National Beamline Facility in the Photon Factory, using the standard setup. The monochromator was a Si(111) channel-cut crystal, detuned such that the intensity incident on the sample was approximately half that measured when the crystal faces were in perfect alignment, in order to reject higher order harmonics. Absorption data were collected for the K-edges of both copper and arsenic, generally in fluorescence mode but sometimes in transmission mode as indicated in Table 7.2. Foils of the appropriate metal were used as energy calibrants. Fluorescence data were collected from undiluted samples held in a 1 mm aluminum spacer with KAPTON™ tape windows, using a Canberra GL 0110S 10-element Ge array detector. For transmission experiments, an ion chamber detector was used, and samples were presented similarly but were diluted to appropriate absorber concentrations with boron nitride. Cupric arsenate was diluted to 20% by weight for the copper experiment, 40% for arsenic; sludge was diluted to 60% for arsenic.

XAS and XAFS data were manipulated and analysed with the XFIT software suite[23], and model XAFS were calculated with the curved-wave multiple scattering program FEFF6.01 [24] using scattering paths of up to four legs. XFIT employs Levenberg-Marquardt iterative nonlinear least squares fitting to optimise selected model parameters such that the difference χ^2 between the calculated and observed XAFS is minimised.

Since the fluorescence detector had ten elements, and each treated wood sample was run twice, there were 20 XAS data sets for all but one of the fluorescence experiments. No systematic differences between channels or runs were observed, so all the data for a particular sample were averaged into a single data set. A typical example is shown in Figure 7.4. After normalisation, the XAFS oscillations were extracted from the XAS through a cubic spline fitting proceedure [Figs. 7.5, 7.6]. At the same time, the data were transformed into photoelectron momenta k in kgÅs^{-1}, and weighted by a factor of k^3 in order to compensate for the decaying amplitude [Fig. 7.7]. The XAFS are clearly visible out to a respectable $k \approx 13$ for copper, 14 for arsenic. Accordingly, the windows for both calculated and observed XAFS were [3k, 13k] or [3k, 14k], with edges smoothed by cosine functions extending a further 0.5 Å.

Figure 7.4

Arsenic XAS for CCA-treated wood; H4 outer layer

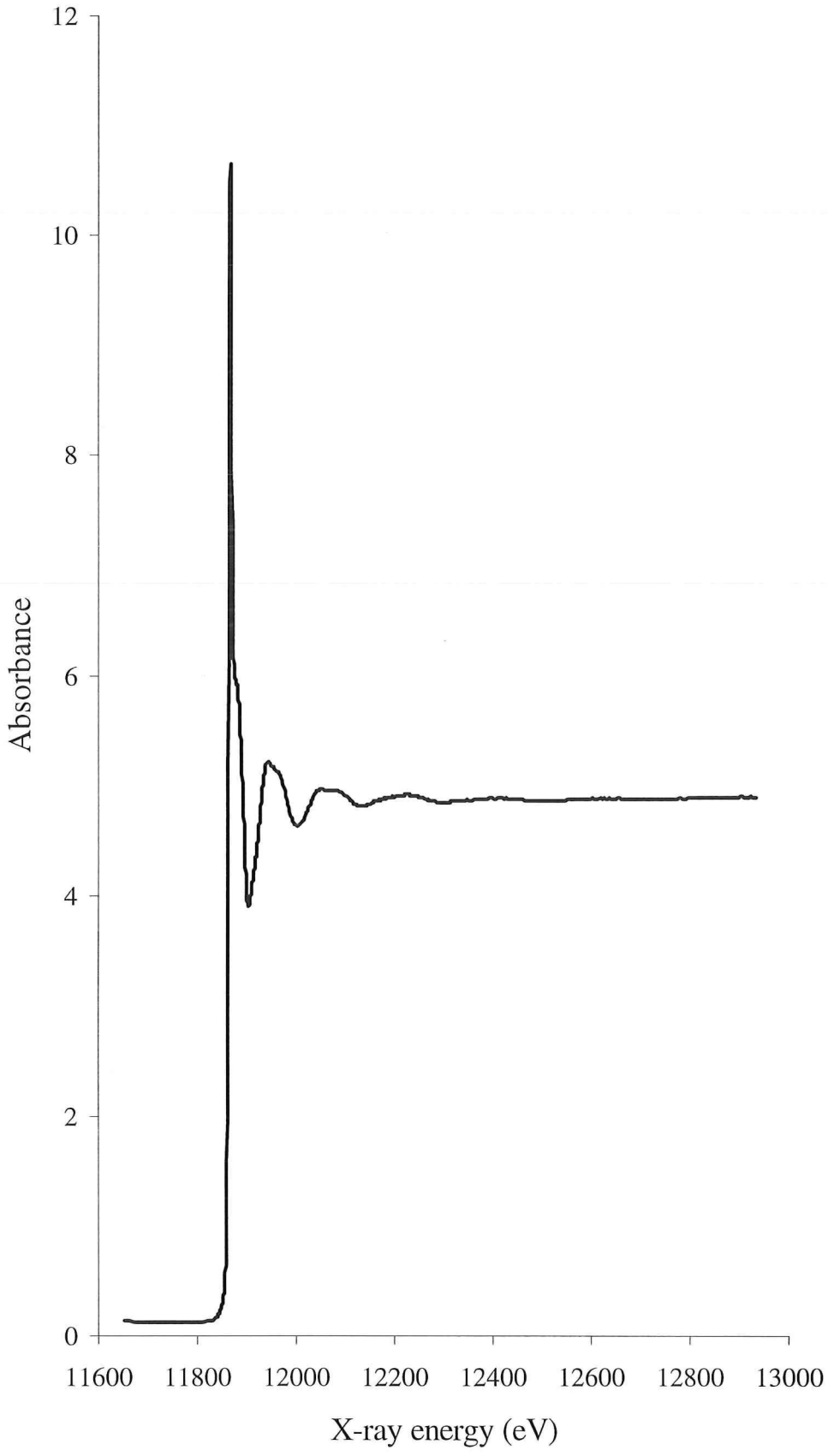


Figure 7.5
Normalised arsenic XAS for
CCA-treated wood; H4 outer layer
Extraction of XAFS via a spline fit to background

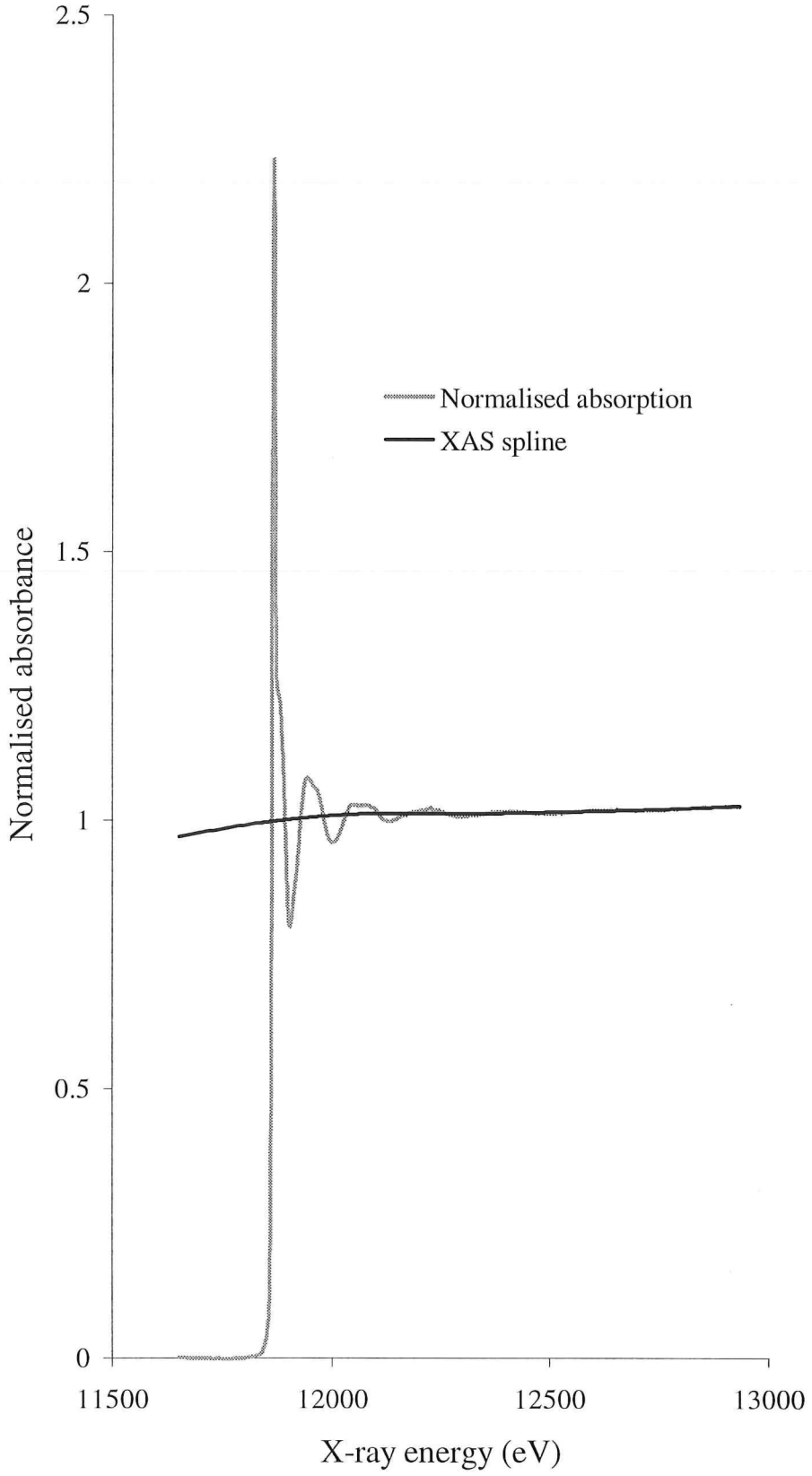


Figure 7.6
Arsenic XAFS for
CCA-treated wood; H4 outer layer

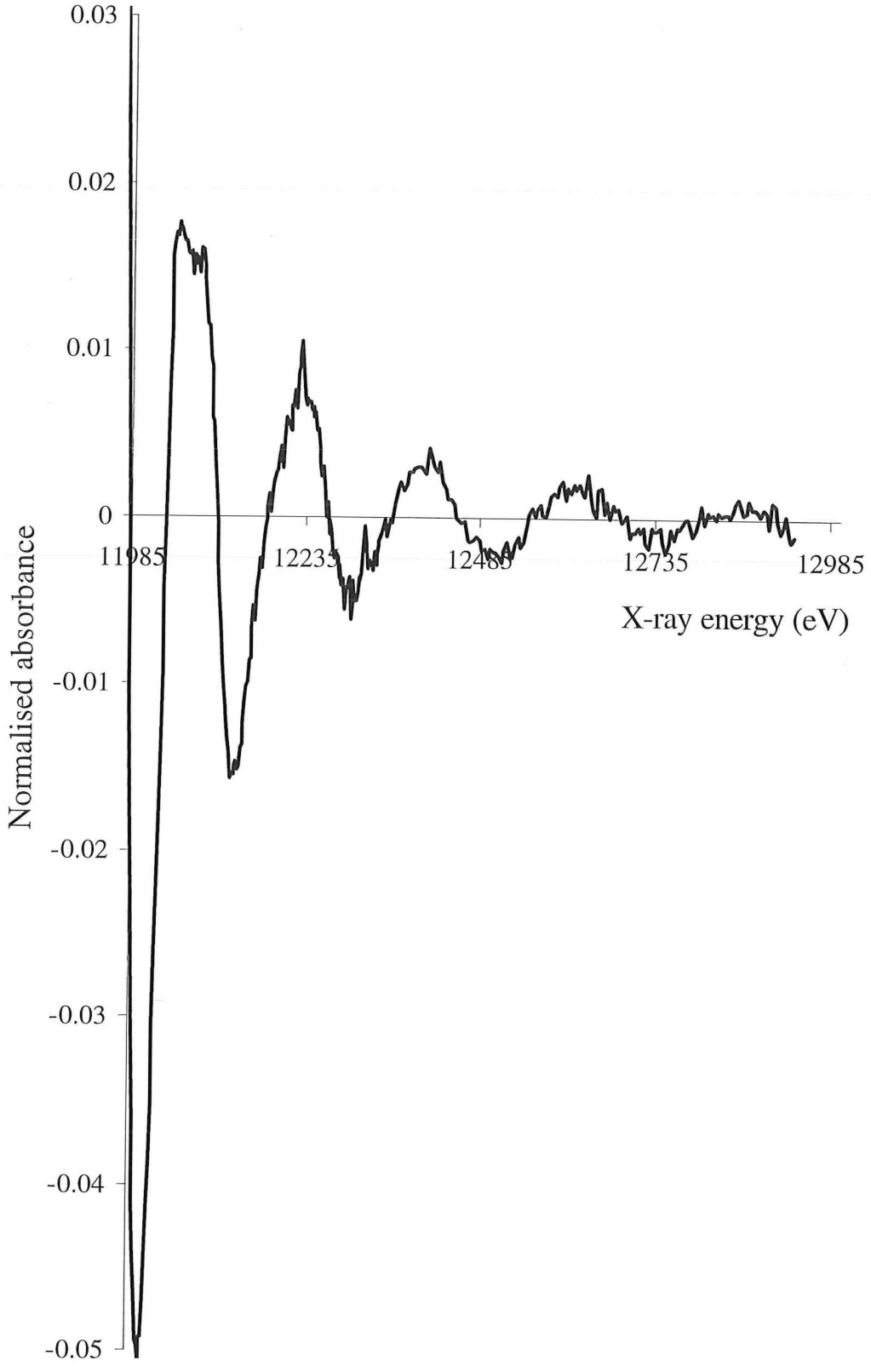
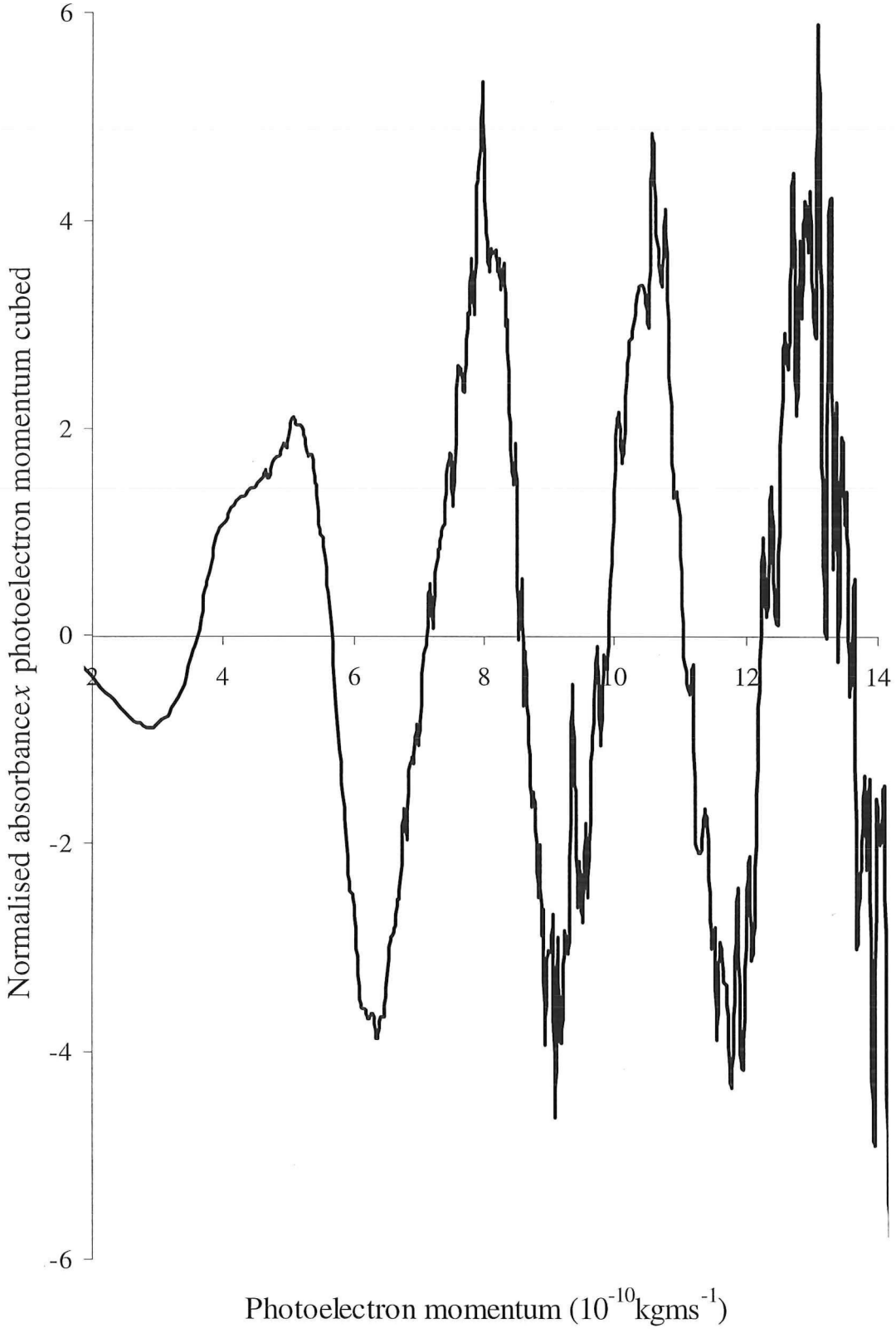


Figure 7.7

Windowed arsenic XAFS for
CCA- treated wood; H4 outer layer
Transformed into k-space, weighted according to k^3



A variety of simple model structures was proposed for each sample, and the theoretical XAFS of these models were constructed *ab initio*. Then the model parameters were refined until the statistical difference between calculated and observed XAFS was minimised. Parameter restraints were not necessary for the best fit models. If any parameters repeatedly refined to zero, excessively large values, or chemically implausible values such as bond lengths < 1 Å, the model was discarded. The goodness-of-fit parameter R, given by

$$R = \frac{\int_{k=0}^{\infty} \left[\chi_{calc}(k) - \chi_{obs}(k)\right]^2 \partial k}{\int_{k=0}^{\infty} \chi_{obs}(k)^2 \partial k}$$

where $\chi_{calc}(k)$ and $\chi_{obs}(k)$ are the calculated and observed filtered EXAFS curves, was also required to be less than 25%.

Standard deviations for most fitted parameters were also obtained, using the Monte Carlo analysis included in XFIT.

Since the XAFS effect is principally dependent on the size of the scatterers and the radial distances between absorber and scatterers, symmetry-equivalent atoms are generally treated as an appropriately weighted single entity or 'shell'. For example, it was found that the arsenic tetrahedra in these experiments were best modelled by a scatterer with phase shift and weight equal to four oxygen atoms at a radial distance just less than 1.7 Å. The model parameters for the best fits are listed in Table 2.

It was confidently expected that cupric arsenate would contain copper (II) directly bound to arsenate. Indeed, Fourier transforms of both copper and arsenic XAFS clearly revealed the presence of heavy next-nearest neighbours. Consequently, modelling began with a simple As-O_4-Cu structure. XFIT's capacity to perform multiple edge data refinements was invoked for cupric arsenate; the model was refined to both copper and arsenic data sets simultaneously. A bond length of 1.68 Å was returned for As-O, consistent with the crystallographic values[25] of 1.61<|As-O|<1.73 in euchroite $Cu_2(OH)AsO_4 \cdot 3H_2O$, or 1.63<|As-O|<1.71 in $FeAsO_4 \cdot 2H_2O$. 1.94 Å for Cu-O is comparable with 1.92<|Cu-O|<2.08 for the four oxygen atoms close to copper in euchroite. Copper (II) would be expected to have a distorted octahedral geometry with two more oxygen atoms further away. In euchroite, they are found at a distance of 2.42-2.72 Å. But in this case, the addition of another oxygen shell does not improve the fit significantly. The last two oxygens may be partially accounted for in the otherwise high occupancy of the oxygen shell in the simple model.

From Chapter 2 it was known that sludge was based on chromic arsenate, so the arsenic spectrum was modelled with an As-O_m-Cr_n structure. The As-O bond length was 1.68 Å, as in the cupric arsenate, |Cr-O| was a reasonable 1.86 Å, and the oxygen shell occupancy was appropriately close to 4. The overall fit was good, although the scale factor S_0^2 was somewhat high. A Cu_p-O_q-**As**-O_m-Cr_n structure produced an equally good result, but was considered unwarranted since the number of copper atoms remained substantially less than 1 during refinement. An **As**-O_q-Cu_p model gave a passable fit, except that |M-O| remained substantially lower than in cupric arsenate or euchroite.

However the copper spectrum of sludge was harder to model. The immediate environment of the copper atoms was simulated by three oxygen shells placed at varying distances along the *x*, *y*, and *z* axes respectively. Regardless of the positions and occupancies of the shells, the only convergent fits ended up with four oxygen atoms and all Cu-O bond lengths equal to 1.92 Å. Despite the poor R-value, no better fit was found with a second shell of arsenic, chromium, or copper. Clearly the copper exists in a variety of environments, unsurprising for a minor constituent of an impure material.

The CCA- treated wood spectra were indistinguishable; thus there is no evidence that the chemical mechanisms of fixation vary between heartwood and sapwood, between salt and oxide formulations, or between H4 and H5 preservative loadings. The arsenic XAFS also match the sludge spectrum, consistent with the expectation that arsenic fixes as chromic arsenate; the As-O_m-Cr_n model refines to even closer fits. Replacing chromium with copper gives a substantially poorer fit; further, the O-M bond length is clearly shorter than the O-Cu distance observed in cupric arsenate. The model shown in Figure 7.8 and Table 7.3 was obtained by fitting to all five data sets simultaneously. Again, the individual fits were virtually identical; the largest parameter standard deviation was only 7.5%, for the occupancy of the oxygen shell in the copper model.

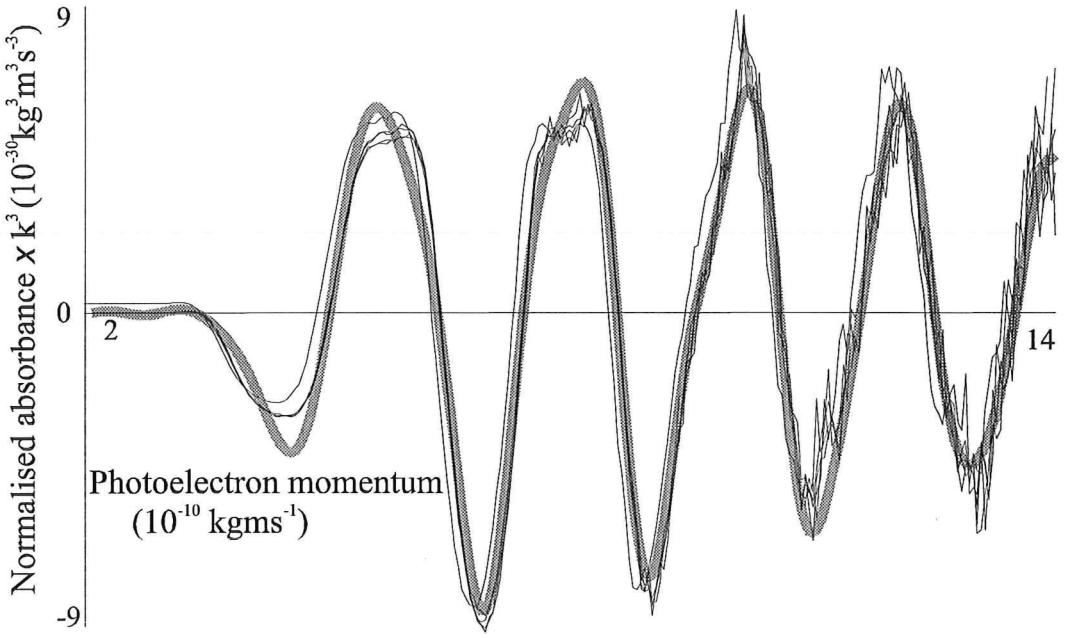
Unlike sludge, the CCA copper XAFS can be adequately modelled. Again, the best fit was close to four oxygen atoms, implying the usual square planar or elongated octahedral geometry. Large second shell atoms are not evident in the Fourier transform and do not improve the model. This is consistent with the expectation that copper ions are complexed to wood, rather than to inorganic species.

In conclusion, these XAFS results are consistent with the hypothesis that arsenic is fixed as chromium (III) arsenate, while copper is complexed to wood constituents. They are inconsistent with the copper arsenates proposed by Dahlgren and Hartford[2,3,4,5] or Pizzi[17].

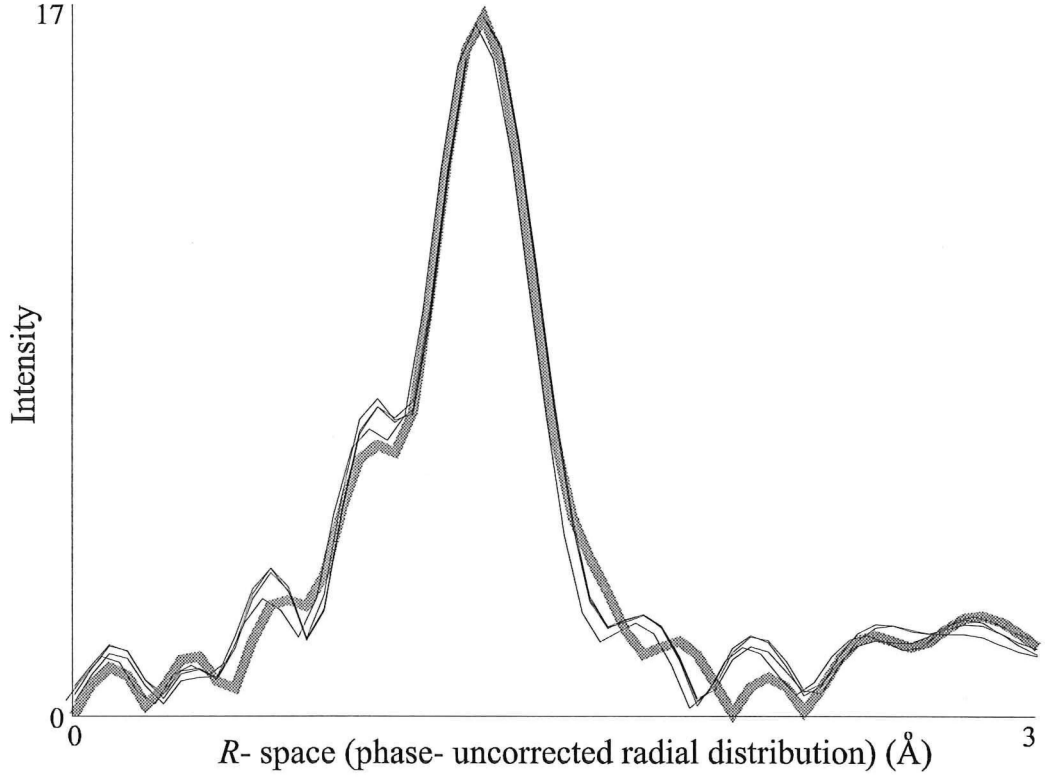
The AC- treated wood flour presented greater problems, particularly since the mechanism of fixation is almost certainly quite different. Starting from the N_2O_2 donor environment indicated by Hughes[8], an oxygen shell was placed along the x coordinate, and a nitrogen shell along y. On the basis of the previous refinements, and the crystal structure for $[Cu(NH_3)_4]SO_4 \cdot 2H_2O$ in which the Cu-N bond length is uniformly 2.05 Å [23], the starting bond lengths were made equal to 1.95 and 2.05 Å respectively. While the coordinates did not vary much during refinement, the relative population of the two model shells was highly unstable. The best model of the NH_4^+ formulation gives a good fit for a roughly even mix and a total coordination number just below 4, consistent with the original hypothesis. But realistically, XAFS is unlikely to be able to distinguish between two shells of such similar atomic number and radial distance. This is clear from the poor refinement of the data for the NH_3 formulation. Theoretically, the minimum resolution is $\Delta|v| > \pi/2k(max) = 0.12$ Å. The fixation of AC would probably be better examined by NMR or even UVA.

Figure 7.8

Arsenic EXAFS for the CCA- treated wood samples and the best fit model for the combined data



Windowed moduli of the Fourier transforms



Calculated

Observed

Table 7.2 Model refinement parameters

Cupric arsenate		Sludge		CCA		*AC (NH_3)*	*AC (NH_4^+)*
EXAFS	Dual	Copper	Arsenic	Copper	Arsenic	*Copper*	*Copper*
R	24.51	**30.62**	14.76	20.06	14.26	*23.49*	*17.03*
Shell 0	*As*	*Cu*	*As*	*Cu*	*As*	*Cu*	*Cu*
E_0	-11.60	-15.25	-11.64	-15.97	-11.78	*-16.61*	*-16.18*
S_0^2	0.7000	0.7208±0.009	**1.086±0.002**	0.6322±0.002	0.8004	*0.9030*	*0.7160*
Shell 1	*O*	*O*	*O*	*O*	*O*	*O*	*O*
N	**5.473**	3.604±0.046	3.830±0.007	4.783±0.016	4.870±0.016	*0.4340*	*2.510*
x	1.679	1.951±0.002	1.680±0.000	1.944±0.001	1.686±0.000	*1.926*	*1.926*
σ^2	0.003139	0.003149	0.004307	0.004292	0.001832	***≈0***	*0.002653*
Shell 2	*Cu*		*Cr*		*Cr*	*N*	*N*
N			5.132±0.067		5.740±0.061	*2.888*	*1.045*
x	2.683		2.975±0.003		2.961±0.001	*0.07363*	*0.1060*
y	1.660		-1.353±0.008		-1.392±0.001	***1.975***	*2.029*
$\lvert v_2-v_b \rvert$	*1.940*		*1.863*		*1.886*	*1.976*	*2.032*
σ^2			0.009789		0.009700	*0.005235*	*0.001688*
E_0	**-12.88**						
S_0^2	**0.4441**						

Non-refined parameters are italicised; parameters refining to unusual values are marked in boldface. The abbreviations are: R, statistical residual measuring goodness-of-fit; E_0, threshold energy correction in eV; S_0^2, many-body amplitude reduction factor; N, number of atoms in the shell; x, y the Cartesian coordinates of the scatterer in Å; σ^2 the Debye-Waller thermal parameter; $\lvert v_2-v_b \rvert$ the distance between second shell scatterer and the atom to which it is bound, in Å. Uncertainties, where given, are estimated standard deviations from the Monte Carlo analysis.

If future extraction work is to be anything other than empirical, it is important to understand the nature of the fixation products. Certainly there are grounds for re-evaluating the somewhat equivocal models proposed to date. A simple combination of wood carboxylate-bound copper, chromic arsenate, and chromic hydroxide is proposed. This model is consistent with the results of a novel and powerful *in situ* investigation using the EXAFS technique.

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Summary and future direction

"It ain't easy being green"- Kermit the Frog

This project has aimed to develop methods capable of recovering the majority of the heavy metal compounds from CCA wastes such as timber treatment plant sludge, degraded working solution, extracts from treated wood, and possibly seriously contaminated materials. The novel electrochemical oxidation process described in Chapter 6 is confidently expected to fulfil that objective. It has been shown that chemical oxidation cannot meet the stringent demands placed upon such a method, and that simple reintroduction into the manufacturing process is counterproductive. A new and effective extraction of arsenate by strong base has been identified, but it is insufficient on its own because it fails to deal with the issue of chromium (III).

This work is also expected to result in several publications. The electrochemical cell is the subject of a patent application by Fernz Timber Protection Ltd. entitled "Process for electrochemical generation of higher oxidation state values from low oxidation state values above zero of transition metal(s) [eg. chromium (VI) from chromium (III) rich chemical waste], including its use in a process separating transition metal values from arsenate moieties [eg. CCA timber treatment plant chemical waste]" A series of three papers "The chemistry of chromated copper arsenate", covering sludge characterisation, fixation reactions and products, and base extraction will be submitted to *Wood Science and Technology*, and eventually followed by a fourth covering treatment of CCA wastes in general. A paper covering the XAFS experiments will be submitted to the *Journal of Materials Science*.

Ultimately the success of the project relies on Fernz Timber Protection and other progressive companies taking the next step, industrial-scale application of these discoveries. Existing problems will not go away regardless of the future extent of CCA treatment or the care with which it is carried out. On the other hand, further pollution might be avoided if new preservatives were developed, perhaps the ammoniacal copper formulations which are already attracting considerable interest. It is an excellent opportunity to continue this productive collaboration between FTP and the University of Canterbury.